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**AOSTRA TECHNICAL PUBLICATION SERIES #14**

**THE ALBERTA OIL SANDS:  
INDUSTRIAL PROCEDURES FOR  
EXTRACTION AND SOME RECENT  
FUNDAMENTAL RESEARCH**

**Loren G. Hepler and Russell G. Smith**



**Alberta**

**OIL SANDS TECHNOLOGY  
AND RESEARCH AUTHORITY**



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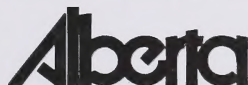




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\* To be published at a future date.

# **THE ALBERTA OIL SANDS: INDUSTRIAL PROCEDURES FOR EXTRACTION AND SOME RECENT FUNDAMENTAL RESEARCH**

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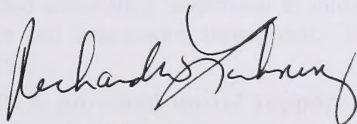
# **AOSTRA TECHNICAL PUBLICATION SERIES**

## **NUMBER 14**

The Alberta Oil Sands Technology and Research Authority (AOSTRA) is pleased to publish this book as part of AOSTRA's continuing program to disseminate information about the oil (tar) sands and heavy oils of Alberta. This book is directly focussed on the hot water process that is used at Syncrude and Suncor for the separation of bitumen from mined oil sands. Synthetic crude that is produced from this bitumen accounts for more than 15% of all the petroleum used in Canada.

Part of AOSTRA's Strategic Research Program was intended to extend the fundamental understanding of certain characteristics of mined oil sands, with the goal of improving the operation of the hot water process for the large-scale industrial separation of bitumen from mined oil sands. This part of the Strategic Research Program was carried out in cooperation with Syncrude Research and the Alberta Research Council. Result of this Strategic Research Program form the basis for some parts of this book, which also contains much useful information about properties of bitumen and reservoir minerals.

This book will be directly useful for the scientists and engineers who are doing research aimed at improving the hot water process or developing alternate liquid-based separation processes. Also, the auxiliary information contained in the book relating to properties of bitumen and reservoir minerals will be useful to those who are working on in situ production processes. This will be the fourteenth book in a series of specially designed technical publications by industrial and academic authors. AOSTRA intends to continue to make available research results, analytical procedures, and engineering data on the properties and behaviour of Alberta's petroleum resources through this publication series.



**R. W. Luhning**  
Vice-Chairman and Executive Director  
Alberta Oil Sands Technology and  
Research Authority

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## PREFACE

For several years the Alberta Oil Sands Technology and Research Authority (AOSTRA) supported a "Strategic Research Program," part of which was focussed on research related to possible improvements in the hot water process that is used for large-scale separation of bitumen from mined oil sands. We began the writing that led to this book with intentions of providing an account of this research, but soon discovered that much of the background information on which this research was based was scattered throughout the technical literature, rather than gathered together in one convenient source. With encouragement from AOSTRA, we expanded the original intention to include preparation of concise accounts of a variety of useful information. More specifically, this book as it now appears has been written for several purposes, as follows:

- (1) To provide some general background (including references to original sources) on the oil (tar) sands of Alberta, with a particular emphasis on the sands that are near enough to the surface to be mined;
- (2) To provide some general background (including references to original sources) on the properties of bitumen;
- (3) To provide detailed information about the hot water process that is now used by Syncrude and Suncor for the large-scale separation of bitumen from mined oil sands;
- (4) To provide some useful background information (including references to original sources) about alternative processes (emphasis on those involving water and/or organic solvents) for separation of bitumen from mined oil sands;
- (5) To provide a summary account of some recent research on the properties of bitumen and reservoir minerals and on the hot water separation process, with particular emphasis on research that was conducted (mostly at Syncrude and the Alberta Research Council) under the auspices of the AOSTRA Strategic Research Program.
- (6) In conclusion, we have also summarized some ideas about possible useful directions for research to be done and related possibilities for process modifications.

Dr. Chu Hsi at AOSTRA provided stimulating leadership in initiating this writing project, and gave us much useful advice and information throughout. We are pleased to acknowledge our substantial debt to Dr. Hsi.

Dr. David Redford at AOSTRA provided initial support and continuing encouragement, for which we are grateful.

Many people at Syncrude Research made both direct and indirect contributions to this writing and to the research on which our writing is based. Dr. Joseph Liu, Dr. Emerson Sanford, and Dr. N.S. Srinivasan provided much useful information and advice, for which we

are grateful. As partly illustrated in Chapter 4, Dr. W.J.R. Tyerman made substantial contributions to the Strategic Research Program; he also provided us with useful advice. We especially thank Brian Turnbull and A. Lemke, who carried out most of the experimental research described in Chapters 5–7.

Dr. Eddy Isaacs at the Alberta Research Council was a participant in the Strategic Research Program. He and Mr. Dzung Nguyen were responsible for arranging facilities to be used by one author (LGH) for writing part of his book and also provided useful information.

We are grateful to Ms. Diane Teppan and Ms. Rachel Recto at AOISTRA for their considerable skill and general spirit of cooperation in handling printing and publication of this book.

Finally, we express our appreciation to Mr. Ross Chow at the Alberta Research Council for writing Chapter 4.

Loren G. Hepler and Russell G. Smith



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# 1

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## *Oil Sands: Background Information*





## **HISTORICAL SUMMARY**

Ferguson (1985) has provided an excellent account (including many references) of the history of Alberta's oil sands; this interesting book also contains considerable technical information, presented clearly and concisely.

Among other historical accounts, we call attention to the following. K.A. Clark (1951) has written about early work in industry and at the Research Council of Alberta (now called the Alberta Research Council). McRory (1982) has provided a brief and clear historical summary. The book by Fitzgerald (1978) contains interesting and colorful accounts of history and various processes (with several mistakes).

A brief chronological summary of the history of the Athabasca oil sands follows.

Henry Kelsey was probably the first European to see the oil sands, in 1719. Later in the same century (1788,1789), Peter Pond and Alexander Mackenzie saw the Athabasca oil sands and noted that the Natives used bitumen for waterproofing and patching their canoes. The first geological description was provided by John Richardson in 1819. Other geological reports followed, including one in 1882 by John Bell, who first mentioned the possibility of a practical hot water process for extracting bitumen from oil sands. In 1913 Sidney C. Ells began his pioneering work, which included some systematic investigations of a hot water process for extracting bitumen from mined oil sands. Then, in 1919, the Government of Alberta established what is now the Alberta Research Council, and in the following year Karl A. Clark began his important work that later provided much of the foundation for the industrial hot water process that is now used for the separation of bitumen from mined oil sands. It was in 1922 that Clark specifically recommended that further work be done to develop the hot water process that Ells had investigated previously. In following years Clark and Sidney M. Blair designed and operated several pilot plants in which their early versions of the hot water process were used to produce bitumen from mined oil sands.

Following the pilot plant work of Clark and Blair, several small (by today's standards) commercial plants were built for recovery of bitumen from mined oil sands. Various combinations of financial and technical troubles (including destructive

fires) kept these plants from being successful, as described in some detail by Ferguson (1985).

The Great Canadian Oil Sands consortium was formed in 1953, leading to construction of the GCOS plant in the years 1964–1968. This plant was authorized to produce at an initial capacity of 31,000 barrels per day. Recent production from Suncor (new name for GCOS) is more than twice as much as originally authorized. Next came the Syncrude plant, which was licensed in 1978 to produce 125,000 barrels of oil per day, subsequently increased to 170,000 barrels per day at present (1991).

## **BITUMEN RESERVES IN ALBERTA**

There have been many estimates of the reserves (defined in several ways) in Alberta. Some of these estimates were as follows.

Pryde (1983) has cited an earlier (1974) report to the U.S. House of Representatives in which it was estimated that there were  $74 \times 10^9$  bbl of bitumen in the Athabasca deposit covered by no more than 150 ft of overburden. This same amount of bitumen in the area that might be mined has been cited by Berkowitz and Speight (1975), Mossop (1980), The Petroleum Resources Communication Foundation (1980), and McRory (1982). Some of the authors mentioned above and also Heron and Spady (1983) and Gray (1988) have provided or quoted estimates of amounts of bitumen that can be recovered from mined oil sands, ranging from  $22 \times 10^9$  to  $38 \times 10^9$  bbl. Estimates of synthetic crude that can be produced from mined oil sands include  $24 \times 10^9$  bbl from McRory (1982),  $26.5 \times 10^9$  bbl from Berkowitz and Speight (1975), and  $28 \times 10^9$  bbl from Gray (1988). To put an average figure of approximately  $26 \times 10^9$  bbl into perspective, we note that The Petroleum Resources Communication Foundation (1980) and McRory (1982) estimated that reserves of conventional oil in Canada amounted to about  $1.1 \times 10^9$  bbl and  $4.5 \times 10^9$  bbl, respectively. Although there are substantial uncertainties in the various estimates, it is clear that the amount of synthetic crude that can be produced from mined oil sands is considerably larger than reserves of conventional oil.

## **GEOLOGY AND MINERALS OF THE ATHABASCA OIL SANDS**

The geological setting of the Athabasca oil sands has been described in some detail by Mossop (1980) and by Wightman et al. (1989). Other, less detailed, accounts of the geology of the Athabasca oil sands have been provided by Berkowitz and Speight (1975), Bichard (1987), Camp (1976a), and Kry et al. (1989). Here we are concerned only with the Wabasca-McMurray deposit, which is near enough the surface to be amenable to open pit mining.

The oil sands deposits considered suitable for mining contain from about 6% to about 18% bitumen. Ores with bitumen contents of more than about 12% are considered (Liu et al., 1989) to be high grade (rich), whereas oil sands with 10 or 11% bitumen and 6 to 9% bitumen are labelled medium grade and low grade (lean), respectively. Total mineral contents range from a low of about 80% for high grade oil sands to a high of about 87% for low grade ore.

Syncrude's analytical methods for determining percent composition have been described in the Syncrude book edited by Bulmer and Starr (1979), in the chapter by Liu et al. (1989), and in recent papers by Dougan (1989) and Thompson (1989). Cloutis (1990) has described a spectroscopic method for investigating bitumen, water, and clay contents in oil sands. Effects of sampling and analytical uncertainties on the determination of major components and such specifics as sulfur content have been investigated and discussed by Wallace et al. (1984ab), Wallace and Kratochvil (1986), Wallace et al. (1988), and Wallace (1988).

The principal mineral present is sand (quartz), having chemical composition  $\text{SiO}_2$ . Bichard (1987), Bowman (1967), Camp (1976ab), and Hocking (1977) have summarized information about other minerals as follows.

"Fine minerals" or "fines" are often defined to be those solids that are smaller than 44 microns, equivalent to passing through a 325 U.S. mesh screen. A large fraction of fines in the oil sands consists of clay minerals (often defined as smaller than 2 microns), principally kaolinite and illite; both of these clays occur with adsorbed or ion-exchanged iron, with the illite usually containing more iron than does the kaolinite. In addition to these two clays, finely divided quartz, montmorillonite, chlorite, feldspar, calcite, and dolomite have been reported (Camp, 1976a) to occur in the fines fraction of minerals in oil sands.

Those fine minerals that are larger than the clays are often called "silt."

Bulmer (1989) and Henry and Wallace (1989) have reported on methods of determining particle sizes in mined Athabasca oil sands.

It has been known for a long time (Bichard, 1987; Clark and Pasternack, 1949; Majid et al., 1982; Sanford, 1983; Smith et al., 1985; and Crickmore et al., 1989) that the amounts and properties of the fine minerals have an important bearing on the recovery of bitumen from mined oil sands. Others who have investigated the fine minerals in Athabasca oil sands include Ignasiak et al. (1983 and 1985), Kessick (1985), Kotlyar et al. (1984, 1985, 1988, and 1990), McIntyre et al. (1986), Sengupta et al. (1988), and Baptista (two papers in 1989). Several of these investigators have shown that iron is involved in the fine mineral-organic interactions.

It is now known that non-bituminous organic matter is present in the Athabasca oil sands, and that such matter (mostly associated with the fine minerals) can have important effects on the processibility of mined oil sands and on the properties of tailings. Several of the publications cited in the last sentence of the paragraph above are concerned with this non-bituminous matter in oil sands. We also call attention to papers by Cyr and Strausz (1984) and by Majid et al. (1986,1990).

Bukka et al. (1991) have investigated the distribution and some effects of minerals on hot water processing of mined Utah tar sand.

In addition to the "light" minerals mentioned above that make up most of the solids present in oil sands, there are smaller amounts of "heavy" minerals of iron, titanium, and other elements, as summarized by Bichard (1987), Camp (1976a), and Kramers and Brown (1976). Trevoiy et al. (1978) have discussed the potential recovery of heavy metals from the Athabasca oil sands. Ityokumbul et al. (1985) have published an account of their efforts to recover these heavy minerals, and have included an extensive list of references to related work.

A selection of properties of minerals found in oil sands is presented in Appendix 1.



## **PROPERTIES OF BITUMEN**

Athabasca oil sands suitable for mining contain from about 6 to about 18 mass percent bitumen.

Several methods of obtaining samples of bitumen to be used for experimental work have been described. As will be noted, there are difficulties associated with each method and with related use of experimental results. In the following paragraphs we will review (in semi-chronological order) several methods that have been proposed for obtaining samples of bitumen to be used in various experimental programs.

Nagra and Armstrong (1978) showed that bitumen can be separated from oil sands by centrifugation through a porous disc. This method has the advantages of no contamination with solvent and minimal loss of light ends. There are two clear disadvantages of this method:

- (1) Recovery of bitumen is significantly less than 100%; it is probable that the most viscous and/or the most polar components are left behind on the sand or other minerals, which means that the recovered sample is not truly representative of the in-place bitumen.
- (2) Some unknown amounts of fines and water are entrained in the recovered bitumen.

Wallace et al. (1984c) have reported on their more recent investigations of centrifugal separation of bitumen from oil sands.

The research group led by Neumann has described (Potoczny et al., 1984ab; and Budziak et al., 1988) their centrifugal method for separation of bitumen from oil sands. As with other centrifugal methods, their method has the advantages of no contact or contamination with solvent and minimal loss of light ends. These researchers have investigated the entrainment of fine solids in the separated bitumen and the fractionation of bitumen that occurs during centrifugal separation. They have also measured the surface (bitumen/air) tensions of samples of bitumen that have been separated in different ways; some of their results are cited later in this chapter and also in Appendix 1.

Henry and Fuhr (1991) have applied room temperature ultracentrifugation (198,000 g) to separation of bitumen from oil sands and have found that approximately 70% of the bitumen can be recovered in this way. It has been found that the centrifuged bitumen contains some emulsified water and fine solids, as well as being slightly enriched in asphaltene components. On the other hand, this method yields bitumen that is not contaminated with any solvent and that has not lost any significant amount of light ends.

Analysts at Syncrude have reviewed the “classical” solvent extraction method for separating the components (bitumen, solids, and water) in oil sands and have also described the Syncrude method, as reported in the book edited by Bulmer and Starr (1979). The classical method is based on extraction with toluene, removal of most of the toluene by heating, and spectrophotometric determination of the amount of toluene that remains. Because the procedure was developed for purposes of analysis, there was no emphasis on obtaining a “pure” sample of bitumen for subsequent use. The more recently developed Syncrude method of separation and subsequent analysis involves extraction with a mixture of toluene and isopropyl alcohol, with the bitumen being determined gravimetrically. This Syncrude separation and analysis method deserves consideration as a potentially useful procedure for obtaining small samples of “representative” bitumen for subsequent experimental investigations.

Many researchers have carried out their investigations using bitumen that has been separated by solvent extraction from mined oil sands, following procedures similar to those described by Vorndran et al. (1980), who investigated various solvents and also various means of separating the solvent and the extracted bitumen. It is partly because of their investigations that many researchers have used toluene as extracting solvent and have removed solvent and water from extracted bitumen by heating to about 150°C. Important considerations in selection of solvent and conditions for removal of the solvent include leaving very little organic residue on the sand, efficient removal of most of the solvent from extracted bitumen, and minimal loss of light ends from the bitumen while the solvent is being removed. For some purposes it is necessary to remove fine minerals by filtration or centrifugation of the (bitumen + solvent) combination before the solvent is removed. Vorndran et al. (1980) have investigated the effects of small amounts of residual solvent and fine minerals on various properties of extracted bitumen, and have observed very large effects on the viscosity.

Williams and Duchowski (1983) have described the Petro-Canada method for solvent extraction of bitumen from oil sands. As with the Syncrude extraction method mentioned above, the emphasis was on analysis of oil sands rather than on obtaining a "representative" sample of bitumen for subsequent use.

Partly because of its ready availability, many researchers have used Syncrude coker feed bitumen. This is exactly the right bitumen to use for investigations of coking or alternative upgrading processes, but is not necessarily best for other investigations, such as those related to separation of bitumen from mined oil sands or those leading to characterization of "representative" bitumen. Coker feed bitumen differs from "representative" bitumen in several respects. First, coker feed bitumen is derived from the bitumen that has been separated from mined oil sands by the industrial hot water process. Such produced bitumen is missing the several percent of bitumen that was not recovered in the industrial process, and it is known that bitumen recovered from tailings has somewhat different properties than does the bitumen that is recovered by way of the hot water process. Second, coker feed bitumen has been exposed to warm air during the separation process and subsequently, leading to slight oxidation. This slight oxidation has negligible effects on some properties, but can have substantial effects on interfacial properties, as reported later in this book. Finally, coker feed bitumen contains some residual naphtha and has lost some light ends.

It must be recognized that we have no way of obtaining "pure, whole" bitumen that contains no non-bituminous matter and that has not lost any of its original constituents. The best that we can do is to be aware of the problems and then try to allow for or minimize the effects of non-bituminous matter or of missing components of the original bitumen.

McRory (1982) has listed bitumens as having densities at 15°C in the range 1.076 to 1.000 kg m<sup>-3</sup>, corresponding to 0 to 10°API. Berkowitz and Speight (1975) and others have reported that Athabasca bitumen has density about 1.02 kg m<sup>-3</sup> at 15°C, corresponding to 6 to 9°API. Results of comparative measurements in Canada and the United States have been reported by Wallace et al. (1988), while a review edited by Wallace (1988) contains data and a useful discussion of experimental methods.

There have been many investigations of the elemental composition of Athabasca bitumen. For example, Bichard (1987, based on earlier investigations) has

listed the following:

83.1% C	10.4–10.9% H
0.5% N	4.7–5.1% S

More recently, Berkowitz and Speight (1975) have provided the following ranges of composition:

$83.3 \pm 0.3\%$ C	$10.3 \pm 0.1\%$ H	$1.1 \pm 0.3\%$ O
$0.4 \pm 0.1\%$ N	$4.9 \pm 0.4\%$ S	

Still more recent reviews or reports of new investigations by Camp (1976a), Hocking (1977), Bunger et al. (1979), McRory (1982), Erskine (1984), Liu et al. (1989), and Hepler (1989) list elemental compositions that are within or very near the ranges specified by Berkowitz and Speight (1975). Some of the variability in reported results is due to real variability in elemental composition of bitumen from different places in the Athabasca region, but some is also due to difficulties in obtaining representative samples and the subsequent analysis, as discussed in some detail by Wallace et al. (1988) and Wallace (1988), who have provided elemental compositions (probably the most accurate and reliable values available) of several samples of bitumen. Some of their values are as follows.

82.1–83.9% C
10.0–11.0% H
0.15–1.38 (mostly 0.4–0.5)% N
3.2–6.2 (mostly 4.2–4.9)% S
17–87 (mostly $\approx 70$ ) mg Ni per kg bitumen
130–310 (mostly $\approx 170$ ) mg V per kg bitumen
230–1100 mg Fe per kg bitumen

Amounts of ash obtained on complete combustion of bitumen reflect the amounts of clays or other fine minerals dispersed in the bitumen and also the amounts of metallic elements that are chemical constituents of bitumen. As indicated above, the principal metals that are chemical constituents of bitumen are iron, vanadium, and nickel, with lesser amounts of other metals such as copper. It is unlikely that the small amounts of these metals are important with respect to recovery of bitumen from mined oil sands, but these small amounts can be important in subsequent upgrading and refining.



Jack et al. (1979,1980) have described their efforts to produce vanadium and other metals from Athabasca coke and ash.

Many investigators have reported average molecular weights of Athabasca bitumen, based upon vapor phase osmometry or measurements of freezing point depression. Some examples of reported average molecular weights for Athabasca bitumen are as follows:

- Berkowitz and Speight (1975): 540–800 g mol<sup>-1</sup>
- Camp (1976a): 539 and 600–700 g mol<sup>-1</sup>
- Selucky et al. (1977): 540 g mol<sup>-1</sup>
- Khan et al. (1984): 620 g mol<sup>-1</sup>
- Mehrotra and Svrcek (1985): 595 g mol<sup>-1</sup>
- Fu et al. (1985): 555 g mol<sup>-1</sup>
- Lu et al. (1986): 544 g mol<sup>-1</sup>
- Fu et al. (1986): 472–620 g mol<sup>-1</sup>
- Wallace (1988) and Wallace et al. (1988): 393–607 g mol<sup>-1</sup>
- Mehrotra et al. (1988): 572 g mol<sup>-1</sup>
- Strausz (1989): 490–620 g mol<sup>-1</sup>
- Wood and Hepler (unpublished): 566 g mol<sup>-1</sup>
- Xu and Hepler (1990): 554 g mol<sup>-1</sup>

Bulmer and Starr (1979), Wallace et al. (1988), and Wallace (1988) have discussed experimental methods for estimating molecular weights of bitumen. It is our opinion that “sample problems” (presence of low molecular weight solvent, or loss of light ends) are a principal source of variability in reported molecular weights.

There has been particular interest in the average molecular weight of the asphaltene fraction. A wide range of values has been reported, as reviewed by Speight et al. (1985).

See Appendix 2 for further discussion of average molecular weights of bitumen and of various components.

The high viscosity of bitumen is responsible for many of the practical difficulties associated with *in situ* production and with the production from mined oil sands that is our interest. Seyer and Gyte (1989) and also Wallace (1988) have provided very useful discussions of experimental methods. Reviews of measured



viscosities have been provided by Seyer and Gyte (1989), who have considered viscosities of bitumens and heavy oils, both “pure” and containing solvents (diluent) or dissolved gases. Seyer and Gyte (1989), Wallace (1988), and an AOSTRA Technical Report (1984) have provided reviews of measured viscosities of Athabasca bitumens.

We call particular attention to the following investigations concerned with the viscosity of Athabasca bitumen.

Dealy (1979) has measured viscosities (also first normal stress differences and viscoelastic functions) of bitumen and has noted that modest concentrations of solvent, asphaltene, and dispersed water have large effects on the viscosity.

Khan et al. (1984) have described theoretically based models of the viscosity of bitumen, and have also presented empirical correlations of the effect of temperature on viscosity. Svrcek and Mehrotra (1988), Mehrotra (1990), Eastick and Mehrotra (1990), and Mehrotra (1991) have extended such investigations. Mehrotra et al. (1992) have provided a review of solubilities of gases in bitumen, and also discussed correlations of viscosity with temperature.

Wallace and Henry (1987) have presented a correlation for correcting the viscosity of solvent-extracted bitumen to obtain the viscosity of corresponding solvent-free bitumen.

Schramm and Kwak (1988) have carried out an extensive investigation of viscosities of Athabasca bitumen and some dispersions of such bitumen. Their experimental viscosities for Athabasca bitumen at several temperatures are as follows.

Temperature/°C	Viscosity/mPa·s
15	$3.8 \times 10^5$
25	$8.4 \times 10^5$
40	$1.4 \times 10^4$
50	$4.7 \times 10^3$
60	$2.0 \times 10^3$
70	$9.3 \times 10^2$
80	$5.0 \times 10^2$

Schramm and Kwak have shown that the well-known Andrade equation provides a simple and reasonably accurate mathematical representation of their viscosities. We write their equation as

$$(1.1) \quad \frac{\text{Viscosity}}{(\text{mPa}\cdot\text{s})} = A \exp\left(\frac{B}{T}\right) = 1.0 \times 10^{-10} \exp\left[1.01 \times \frac{10^4}{T}\right]$$

where  $T$  is the temperature expressed in kelvins. Schramm and Kwak have also shown that equations of the same type with larger values of the  $A$  parameter and nearly the same values of  $B$  provide good representations of viscosities reported by two other investigators.

In another review (Hepler, unpublished) a graph of the logarithm of viscosity against  $1/T$  has been constructed, using all of the viscosities cited in the various publications mentioned above. It is clear that there is a reasonably linear correlation at temperatures up to nearly  $100^\circ\text{C}$ . This linear correlation is summarized by

$$(1.2) \quad \frac{\text{Viscosity}}{(\text{mPa}\cdot\text{s})} = (4 \pm 3) \times 10^{-10} \exp\left[(1.01 \pm 0.1) \times \frac{10^4}{T}\right]$$

in which  $\pm$  values have been chosen so that most of the reported viscosities are included in the ranges represented by the equation. A similar equation with larger  $A$  and smaller  $B$  can be used to represent viscosities at higher temperatures, or a more complicated equation can be used to represent viscosities over the entire range of temperatures at which such measurements have been made.

Schramm and Kwak (1988) have also provided  $A$  and  $B$  values for mixtures of bitumen with naphtha.

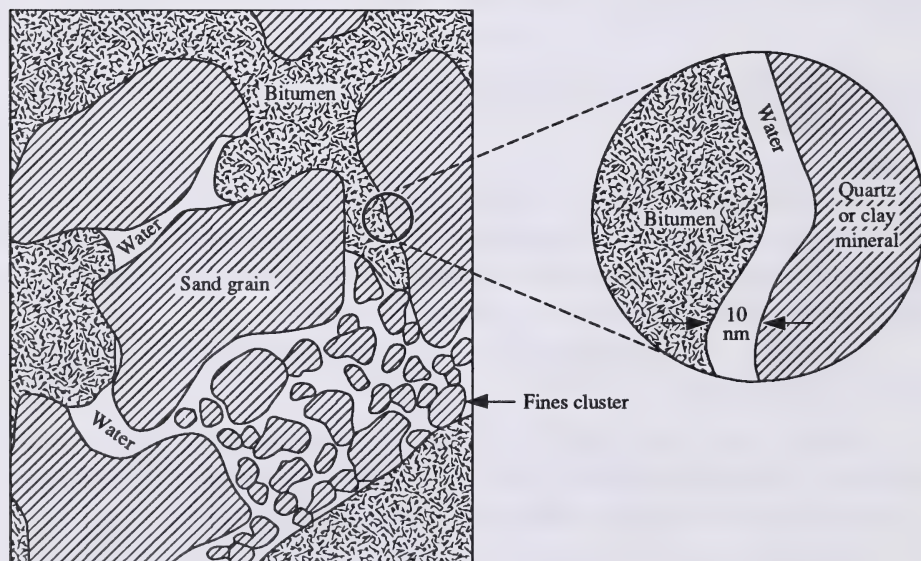
Hupka et al. (1983,1987) and Yang et al. (1989) have reported on their interesting investigations of the importance of viscosity of bitumen (and related role of organic diluent) on hot water processing of Utah tar sands.

Heats of combustion (constant volume,  $\Delta U$ ) and specific heats of bitumen and other substances have been reviewed by Hepler (1989). A selection of values of these thermodynamic properties is presented in Appendix 1.

Some interfacial properties of bitumen, which are of considerable importance in the separation of bitumen from mined oil sands, are discussed later in this chapter and also in subsequent chapters.

## A PHYSICAL PICTURE OF OIL SANDS

As will be seen in later chapters, a physical picture or model of oil sands can serve as part of the basis for a model or theory of the processes leading to separation of bitumen from the oil sands. A simple schematic picture of oil sands that is based on work of several investigators including Cottrell (1963), Dusseault and Morgenstern (1978), Mossop (1980), Takamura (1982 and 1985), Ferguson (1985), and Schramm and Smith (1985) is illustrated in Figure 1.1. Takamura (1982) and Takamura and Chow (1983) have carried out calculations related to the model shown in Figure 1.1; these calculations provide some understanding of the proportions of sand, fine minerals, bitumen, and water in various grades of oil sands and their influence on recovery. We return to this subject later in this book.



**Figure 1.1.** Schematic illustration of the arrangement of bitumen, water, sand, and fine minerals in a typical sample of Athabasca oil sand.

## **SURFACE AND INTERFACIAL PROPERTIES**

The surface and interfacial properties of the constituents of oil sands are of great importance in the separation and recovery of bitumen from mined oil sands.

Takamura and Isaacs (1989) have reviewed this important subject.

We also call attention to the following reports.

Bowman (1967) has provided a useful review of many aspects of the Athabasca oil sands, with particular emphasis on the interfacial properties. Subsequently, Leja and Bowman (1968) reported on their application of thermodynamics to interfacial properties in oil sands.

Speight and Moschopedis (1977,1978) and Moschopedis et al. (1980) have reported results of their investigations of factors (including surface/interfacial tensions) affecting recovery of bitumen by the hot water process. Some of these and also other results are included in another report by Speight and Moschopedis (1980).

Interfacial properties in relation to emulsions have been considered by Levine and Sanford (1985), in two papers by Levine et al. (1989), and in a book edited and partly written by Schramm (1992). Tyerman (1989) has investigated the interaction of surfactants with dispersions of bitumen, solvent, solids, and water.

Misra et al. (1981) have reported on the surface chemistry features that are important in processing Utah tar sand.

For the surface tension (liquid-air interfacial tension) of Athabasca bitumen we have experimental results from Bowman (1967) as quoted by Mehrotra et al. (1985) and from Isaacs and Smolek (1983) as follows.

Temperature/°C	Surface tension/(mJ m <sup>-2</sup> or mN m <sup>-1</sup> )	
64	23.6	29.6
75	22.6	28.3
104	19.0	25.6
112	18.1	25.0



Bowman's results (centre column) are for bitumen that was solvent-extracted from mined oil sands, whereas the results of Isaacs and Smolek (right hand column) are for bitumen that was separated from mined oil sands by the commercial hot water process. It is likely that the different results above are due mostly to differences in the bitumens rather than to experimental errors in the measurements of surface tensions.

As previously mentioned, Potoczny et al. (1984ab) have investigated the surface tension of Athabasca bitumen that was obtained by centrifugation of mined oil sands. Their surface tensions (liquid-air interfacial tensions) of Athabasca bitumen obtained by centrifugation are as follows.

Temperature/°C	Surface tension/(mJ m <sup>-2</sup> or mN m <sup>-1</sup> )
40	32.0
50	31.2
60	30.4
70	29.7
80	28.9
90	28.2

These surface tensions can be summarized accurately by the equation

$$(1.3) \quad \frac{\text{Surface tension}}{(\text{mJ m}^{-2} \text{ or mN m}^{-1})} = 35 - 0.076 \frac{t}{^{\circ}\text{C}}$$

These same researchers (Potoczny, 1984a,b) have also measured surface tensions of Athabasca bitumen obtained by extraction with several solvents. Results of all these measurements on various samples of solvent-extracted Athabasca bitumen can be summarized reasonably accurately by

$$(1.4) \quad \frac{\text{Surface tension}}{(\text{mJ m}^{-2} \text{ or mN m}^{-1})} = 29 - 0.074 \frac{t}{^{\circ}\text{C}}$$



These equations (1.3) and (1.4) show (for any temperature in their range) that the surface tension of solvent extracted Athabasca bitumen is smaller than the surface tension of bitumen obtained by their centrifugation method.

We note that the results of Potoczny et al. (1984ab) for centrifuged bitumen are close to those of Isaacs and Smolek (1983) while their results for solvent extracted bitumen are close to those of Bowman (1967).

Interfacial tensions of Athabasca bitumen-water and (organic solvent + bitumen)-water systems have been investigated by Isaacs and Smolek (1983), Isaacs and Morrison (1985), Isaacs et al. (1989), and Dobrogowska and Hepler (unpublished). Khulbe et al. (1985) have investigated interfacial tensions of Lloydminster heavy oil and its constituents against aqueous alkaline solutions, with some conclusions that are relevant to our concern with Athabasca bitumen.

Schramm and Hepler (submitted for publication) have investigated interfacial tensions of aqueous suspensions of clays.

Results of some of the investigations mentioned in the two preceding paragraphs are reported in Chapter 4, where interfacial tensions are discussed in relation to other properties.

As reported and discussed in later chapters, the bitumen-water interfacial tension is markedly dependent on pH of the aqueous phase. The decrease in interfacial tension at high pH is almost certainly due to formation of natural surfactants by reaction of aqueous hydroxide ions with weakly acidic constituents of the bitumen. As also discussed in later chapters, considerable progress has been made in identifying the surfactants that are formed in this way and in relating the concentrations of these surfactants to such important factors as the amounts of sodium hydroxide needed to obtain maximum recovery of bitumen.

Although bulk properties (such as specific heat) of bitumen are not much influenced by presence of small amounts of fine minerals or by slight oxidation of the bitumen, interfacial properties can be affected substantially by fine minerals or by slight oxidation.

Mehrotra et al. (1985) have presented a procedure for predicting the surface tension of Athabasca bitumen.

As stated in the review by Takamura and Isaacs (1989), electrophoretic measurements are one of the most useful means of investigating the electrical properties of interfaces. In this connection, we call attention to a recent report by Hupka and Miller (1991), who have applied electrophoretic measurements to characterization of Utah tar sands and have cited a number of useful references to related earlier work. Further discussions of electrophoretic measurements and results are included in later chapters in this book.

Hepler et al. (1987) have reviewed water soluble substances (some of which are surface-active) derived from bitumens and heavy oils. Related information about water soluble substances has also been summarized in Kasperski's review (1992) of oil sands tailings.

Various investigators already cited and also Ali (1978) have discussed the role of natural surfactants in the hot water process for separating bitumen from mined oil sands. Several extensive investigations at Syncrude by Schramm and Smith (cited and discussed later in this book) have been concerned with the production of surfactants by reaction of sodium hydroxide with bitumen and with the role of these surfactants in the hot water process.

## REFERENCES

- Ali, L.H. Surface-active agents in the aqueous phase of the hot-water flotation process for oil sands, *Fuel* (1978) 57, 357–360.
- AOSTRA Technical Report, *The thermodynamic and transport properties of bitumens and heavy oils*, Alberta Oil Sands Technology and Research Authority, Edmonton (1984).
- Baptista, M.V. Role of the exchangeable cations of oil sand clays in oil sands processing — part 1. Batch tests, *AOSTRA J. Research* (1989) 5, 237–241.
- Baptista, M.V. Role of the exchangeable cations and iron-amorphous coatings of the oil sand solids in oil sand processing — part 2. Pilot and plant tests, *AOSTRA J. Research* (1989) 5, 243–256.
- Berkowitz, N., and Speight, J.G. The oil sands of Alberta, *Fuel* (1975) 54, 138–149.

- Bichard, J.A. *Oil sands composition and behavior research: the research papers of John A. Bichard, 1957–1965*, (1987) Alberta Oil Sands Technology and Research Authority, Edmonton.
- Bowman, C.W. Molecular and interfacial properties of Athabasca tar sands, *Proceedings, 7th World Petroleum Congress* (1967) 3, 583–603.
- Budziak, C.J., Vargha-Butler, E.I., Hancock, R.G.V., and Neumann, A.W. Study of fines in bitumen extracted from oil sands by heat-centrifugation, *Fuel* (1988) 67, 1633–1638.
- Bukka, K., Miller, J.D., Hanson, F.V., and Oblad, A.G. Mineral matter distribution during the hot water processing of Utah tar sand, *AOSTRA J. Research* (1991) 7, 101–109.
- Bulmer, J.T. Particle size analysis using direct dispersion techniques, *AOSTRA J. Research* (1989) 5, 257–264.
- Bulmer, J.T., and Starr, J. eds., *Syncrude analytical methods for oil sand and bitumen processing*, (1979) Syncrude Canada Ltd., Edmonton.
- Bunger, J.W., Thomas, K.P., and Dorrence, S.M. Compound types and properties of Utah and Athabasca tar sand bitumens, *Fuel* (1979) 58, 183–195.
- Camp, F.W. *The tar sands of Alberta, Canada*, 3rd ed., (1976a), Cameron Engineers, Inc., Denver.
- Camp, F.W. Processing Athabasca tar sands — tailings disposal, (1976b), Symposium on Tar Sands, 26th Canadian Chemical Engineering Conference, Toronto.
- Clark, K.A. Opening remarks to the oil-recovery session, *Proceedings: Athabasca oil sands conference*, Government of Alberta, (1951) Edmonton, pp. 183–184.
- Clark, K.A., and Pasternack, D.S. The role of very fine mineral matter in the hot water separation process as applied to Athabasca bituminous sand, *Research Council of Alberta* (1949) Report No. 53.
- Cloutis, E.A. Identification, detection and characterization of individual tar sand phases using diffuse reflectance spectroscopy (0.35–2.6  $\mu\text{m}$ ), *AOSTRA J. Research* (1990) 6, 17–27.

- Cottrell, J.H. Development of an anhydrous process for oil-sand extraction, in *The K.A. Clark volume*, (1963) ed. M.A. Carrigy, Information Series No. 45, Research Council of Alberta, Edmonton.
- Crickmore, P.J., Schutte, R., and Cleaver, J.A.S. The yield-grade relationship in the extraction of bitumen from oil sands, *AOSTRA J. Research* (1989) 5, 195–201.
- Cyr, T.D., and Strausz, O.P. Bound carboxylic acids in the Alberta oil sands, *Org. Geochem.* (1984) 7, 127–140.
- Dealy, J.M. Rheological properties of oil sands bitumens, *Can. J. Chem. Eng.* (1979) 57, 677–683.
- Dobrogowska, C., and Hepler, L.G. Unpublished research, University of Alberta.
- Dougan, P.D. Near infra-red analysis: its potential application in oil sand processing, *AOSTRA J. Research* (1989) 5, 203–209.
- Dusseault, M.B., and Morgenstern, N.R. Shear strength of Athabasca oil sands, *Can. Geotech. J.* (1978) 15, 216–238.
- Eastick, R.R., and Mehrotra, A.K. Viscosity data and correlation for mixtures of bitumen fractions, *Fuel Proc. Technol.* (1990) 26, 25–37.
- Erskine, H.L. Suncor hot water process, Chapter 5-1 in *Handbook of synfuels technology*, ed. R.A. Meyers (1984), McGraw-Hill, New York.
- Ferguson, B.G. *Athabasca oil sands: northern resource exploration*, (1985), Alberta Culture, Edmonton.
- Fitzgerald, J.J. *Black gold with grit*, (1978) Gray's Publishing Ltd., Sidney, B.C.
- Fu, C.-T., Puttagunta, V.R., and Vilcsak, G. Vapour-liquid equilibrium properties for pseudo-binary mixtures of CO<sub>2</sub>-Athabasca bitumen and N<sub>2</sub>-Athabasca bitumen, *AOSTRA J. Research* (1985) 2, 73–81.
- Fu, C.-T., Puttagunta, R., Baumber, L., and Hsi, C. Pseudo-critical properties of heavy oils and bitumens, *Fluid Phase Equil.* (1986) 30, 281–295.



- Gray, G.R. Bitumen, *The Canadian encyclopedia*, (1988) vol. 1, pp. 233–235. Hurtig Publ. Inc., Edmonton.
- Henry, D.J., and Fuhr, B.J. Preparation of bitumen from oil sand by ultracentrifugation, presented at Eastern oil shale symposium, November 13–15, (1991) Lexington, Kentucky. Submitted for publication.
- Henry, D., and Wallace, D. Methods used to determine particle size distribution of oil sand solids, *AOSTRA J. Research* (1989) 5, 337–350.
- Hepler, L.G. Thermodynamic and thermochemical properties, Chapter 4 in *AOSTRA technical handbook on oil sands, bitumens and heavy oils*, (1989), ed. L.G. Hepler and C. Hsi, Alberta Oil Sands Technology and Research Authority, Edmonton.
- Hepler, L.G. Unpublished, AOSTRA Strategic Program.
- Hepler, L.G., Dobrogowska, C., and Kasperski, K. Water soluble substances from heavy oils and tar sands bitumens — an overview, in *Oil in freshwater: chemistry, biology, countermeasure technology*, (1987), ed. J. H. Vandermeulen and S.E. Hrudey. Pergamon Press, New York (1987).
- Heron, J.J., and Spady, E.K. Oil sands: the Canadian experience, *Ann. Rev. Energy* (1983) 8, 137–163.
- Hocking, M.B. The chemistry of oil recovery from bituminous sands, *J. Chem. Educ.* (1977) 54, 725–729.
- Hupka, J., Miller, J.D., and Cortez, A. Importance of bitumen viscosity in the hot water processing of domestic tar sands, *Mining Eng.* (1983) 35, 1635–1641.
- Hupka, J., Oblad, A.G., and Miller, J.D. Diluent-assisted hot-water processing of tar sands, *AOSTRA J. Research* (1987) 3, 95–102.
- Hupka, J., and Miller, J.D. Electrophoretic characterization and processing of Asphalt Ridge and Sunnyside tar sands. *Int. J. Mineral Proc.* (1991) 31, 217–231.
- Ignasiak, T.M., Kotlyar, L., Longstaffe, F.J., Strausz, O.P., and Montgomery, D.S. Separation and characterization of clay from Athabasca asphaltene, *Fuel* (1983) 62, 353–362.



- Ignasiak, T.M., Zhang, Q., Kratochvil, B., Maitra, C., Montgomery, D.S., and Strausz, O.P. Chemical and mineral characterization of the bitumen-free Athabasca oil sands related to the bitumen concentration in the sand tailings from the Syncrude batch extraction test, *AOSTRA J. Research* (1985) 2, 21–35.
- Isaacs, E.E., and Smolek, K.F. Interfacial tension behavior of Athabasca bitumen/aqueous surfactant systems, *Can. J. Chem. Eng.* (1983) 61, 233–240.
- Isaacs, E.E., and Morrison, D.N. Interfacial films at the Athabasca bitumen/water interface, *AOSTRA J. Research* (1985) 2, 113–119.
- Isaacs, E.E., Maunder, J.D., and Li, J. Interfacial tension of heavy oil-aqueous systems at elevated temperatures, Chapter 17 in *Oil-field chemistry: enhanced production and stimulation*, (1989) ed. J.K. Borchardt and T.F. Yen, ACS Symposium Series No. 396, Washington.
- Ityokumbul, M.T., Kosaric, N., Bulani, W., and Cairns, W.L. Froth flotation for the beneficiation of heavy minerals from oil sands tailings, *AOSTRA J. Research* (1985) 2, 59–66.
- Jack, T.R., Sullivan, E.A., and Zajic, J.E. Leaching of vanadium and other metals from Athabasca oil sands coke and coke ash, *Fuel* (1979) 58, 589–594.
- Jack, T.R., Sullivan, E.A., and Zajic, J.E. The release of vanadium from Athabasca oil sands cokes by leaching techniques, *Can. Mining and Metall. Bull.* (1980, May) 1–6.
- Kasperski, K.L. A review of properties and treatment of oil sands tailings, *AOSTRA J. Research* (1992) 8, 11–53.
- Kessick, M.A. Complex acids and their interaction with clays in oil sands slimes, in *Surface phenomena in enhanced oil recovery*, (1981) ed. D. O. Shah, Plenum Publ. Corp., New York.
- Khan, M.A.B., Mehrotra, A.K., and Svrcek, W.Y. Viscosity models for gas-free Athabasca bitumen, *J. Can. Petrol. Technol.* (1984, May–June) 23, 47–53.

- Khulbe, K.C., Hornof, V., and Neale, G. Interfacial activity of heavy oil and its maltene constituents against caustic solutions, *AOSTRA J. Research* (1985) 2, 95–101.
- Kotlyar, L.S., Sparks, B.D., and Kodama, H. Some chemical and mineralogical properties of fine solids derived from oil sands, *AOSTRA J. Research* (1984) 1, 99–106.
- Kotlyar, L.S., Sparks, B.D., and Kodama, H. Isolation of inorganic matter-humic complexes from Athabasca oil sands, *AOSTRA J. Research* (1985) 2, 103–111.
- Kotlyar, L.S., Sparks, B.D., and Kodama, H. Properties of fines size fractions in relation to the distribution of humic-inorganic matter complexes in Athabasca oil sands, *AOSTRA J. Research* (1988) 4, 277–285.
- Kotlyar, L.S., Sparks, B.D., and Kodama, H. Isolation and characterization of organic-rich solids present in Athabasca tailings pond sludge, *AOSTRA J. Research* (1990) 6, 41–51.
- Kramers, J.W., and Brown, R.A.S. Survey of heavy minerals in the surface-mineable area of the Athabasca oil sand deposit, *Can. Mining and Metall. Bull.* (1976, December) 1–8.
- Kry, P.R., Gronseth, J.M., and Morgenstern, N.R. Geotechnical properties, Chapter 8 in *AOSTRA technical handbook on oil sands, bitumens and heavy oils*, (1989), ed. L.G. Hepler and C. Hsi, Alberta Oil Sands Technology and Research Authority, Edmonton.
- Leja, J., and Bowman, C.W. Application of thermodynamics to the Athabasca tar sands, *Can. J. Chem. Eng.* (1968) 46, 479–481.
- Levine, S., Bowen, B.D., and Partridge, S.J. Stabilization of emulsions by fine particles. I. Partitioning of particles between continuous phase and oil/water interface, *Colloids and Surfaces* (1989) 38, 325–343.
- Levine, S., Bowen, B.D., and Partridge, S.J. Stabilization of emulsions by fine particles. II. Capillary and van der Waals forces between particles, *Colloids and Surfaces* (1989) 38, 345–364.

- Levine, S., and Sanford, E. Stabilization of emulsion droplets by fine powders, *Can. J. Chem. Eng.* (1985) 63, 258–268.
- Liu, J.K., Bulmer, J.T., Cooley, J.M., Crickmore, B.D., Hall, R.H., and Hoyle, R.E. Analytical methods, Chapter 2 in *AOSTRA technical handbook on oil sands, bitumens and heavy oils*, (1989), ed. L.G. Hepler and C. Hsi, Alberta Oil Sands Technology and Research Authority, Edmonton.
- Lu, B.C.-Y., Chung, W.K., Adachi, Y., and Boublik, T. Correlation and prediction of solubilities of gases in Athabasca bitumen, *AOSTRA J. Research* (1986) 2, 139–146.
- Majid, A., Sirianni, A.F., and Ripmeester, J.A. Comparative study of three laboratory methods for the extraction of bitumen from oil sands, *Fuel* (1982) 61, 477–479.
- Majid, A., and Ripmeester, J.A. Characterization of unextractable organic matter associated with heavy minerals from oil sand, *Fuel* (1986) 65, 1714–1727.
- Majid, A., Sparks, B.D., and Ripmeester, J.A. Characterization of insoluble organic matter associated with non-settling clay minerals from Syncrude sludge pond tailings, *Fuel* (1990) 69, 145–150.
- McIntyre, D.D., Montgomery, D.S., and Strausz, O.P. Carboxylic acids bound to the mineral matter in heavy cretaceous oils of Alberta, *AOSTRA J. Research* (1986) 2, 223–231.
- McRory, R.E. *Oil sands and heavy oils of Alberta*, (1982) Alberta Energy and Natural Resources, Edmonton.
- Mehrotra, A.K. Development of mixing rules for predicting the viscosity of bitumen and its fractions blended with toluene, *Can. J. Chem. Eng.* (1990) 68, 839–848.
- Mehrotra, A.K. Modeling temperature and composition dependence for the viscosity of diluted bitumens, *J. Petrol. Sci. and Eng.* (1991) 5, 261–272.
- Mehrotra, A.K., and Svrcek, W.Y. Viscosity, density and gas solubility data for oil sand bitumens. Part I: Athabasca bitumen saturated with CO and C<sub>2</sub>H<sub>6</sub>, *AOSTRA J. Research* (1985) 1, 263–268.

- Mehrotra, A.K., Yee, C-T., and Svrcek, W.Y. Prediction of surface tension of Athabasca bitumen, *Can. J. Chem. Eng.* (1985) 63, 340–343.
- Mehrotra, A.K., Svrcek, W.Y., Fu, C-T., and Puttagunta, V.R. Reconciliation of gas-solubility data, *AOSTRA J. Research* (1988) 4, 237–243.
- Mehrotra, A.K., Svrcek, W.Y., Hepler, L.G., Xu, Y., and Fu, C-T. Comments on “Solubility of Carbon Dioxide in Tar Sand Bitumens: Experimental Determination and Modeling”, *Ind. Eng. Chem. Res.* (1992) 31, 1422–1423.
- Misra, M., Aguilar, R., and Miller, J.D. Surface chemistry features in the hot water processing of Utah tar sand, *Sep. Sci. and Technol.* (1981) 16, 1523–1544.
- Moschopedis, S.E., Schulz, K.F., Speight, J.G., and Morrison, D.N. Surface-active materials from Athabasca oil sands, *Fuel Proc. Technol.* (1980) 3, 55–61.
- Mossop, G. D. Geology of the Athabasca oil sands, *Science* (1980) 207, 145–152.
- Nagra, S.S., and Armstrong, D.A. Separation of bitumen from Athabasca oil sand by centrifugation through a porous disc, (1978) Report to Alberta Oil Sands Technology and Research Authority, Edmonton.
- Potoczny, Z.M., Vargha-Butler, E.I., Zubovits, T.K., and Neumann, A.W. Surface tension of bitumen. I. Temperature dependence, *AOSTRA J. Research* (1984a) 1, 107–115.
- Potoczny, Z.M., Vargha-Butler, E.I., Zubovits, T.K., and Neumann, A.W. Surface tension of bitumen. II. Solvent and fractionation effects, *AOSTRA J. Research* (1984b) 1, 117–120.
- Pryde, P.R., *Nonconventional energy resources*, (1983) John Wiley & Sons, New York.
- Sanford, E. C. Processibility of Athabasca oil sand: Interrelationship between oil sand fine solids, process aids, mechanical energy and oil sand age after mining, *Can. J. Chem. Eng.* (1983) 61, 554–567.
- Schramm, L.L. ed., *Emulsions: fundamentals and applications in the petroleum industry*, (1992) Advances in Chemistry Series 231, American Chemical Society, Washington, D.C.



- Schramm, L.L., and Smith, R.G. The influence of natural surfactants on interfacial charges in the hot-water process for recovering bitumen from the Athabasca oil sands, *Colloids and Surfaces* (1985) 14, 67–85.
- Schramm, L.L., and Kwak, J.C.T. The rheological properties of an Athabasca bitumen and some bituminous mixtures and dispersions, *J. Can. Petrol. Technol.* (1988, January–February) 27, 26–35.
- Schramm, L.L., and Hepler, L.G. Surface and interfacial tensions of aqueous dispersions of charged colloidal particles (clays). Submitted for publication.
- Selucky, M.L., Chu, Y., Ruo, T., and Strausz, O.P. Chemical composition of Athabasca bitumen, *Fuel* (1977) 56, 369–381.
- Sengupta, S., Hall, E.S., and Tollefson, E.L. Isolation and characterization of nonbituminous organic materials which may interfere with recovery of bitumen from oil sands, in *Proceedings: The fourth UNITAR/UNDP international conference on heavy crude and tar sands*, vol. 5, (1988) ed. R.F. Meyer and E.J. Wiggins, Alberta Oil Sands Technology and Research Authority, Edmonton.
- Seyer, F.A., and Gyte, C.W. Viscosity, Chapter 7 in *AOSTRA technical handbook on oil sands, bitumens and heavy oils*, (1989), ed. L.G. Hepler and C. Hsi, Alberta Oil Sands Technology and Research Authority, Edmonton.
- Smith, M.M., Ehrlich, R., and Hardin, A. A study of Fourier grain shape analysis and batch recoveries of bitumen from Athabasca oil sands, *AOSTRA J. Research* (1985) 1, 245–253.
- Speight, J.G., and Moschopedis, Factors affecting bitumen recovery by the hot water process, *Fuel Proc. Technol.* (1977/1978) 1, 261–268.
- Speight, J.G., and Moschopedis, S.E. Surface and interfacial phenomena related to the hot water processing of Athabasca oil sands, *Information Series 86* (1980), Alberta Research Council, Edmonton.
- Speight, J.G., Wernick, D.L., Gould, K.A., Overfield, R.E., Rao, B.M.L., and Savage, D.W. Molecular weight and association of asphaltenes: A critical review, *Rev. Inst. Francais Petrol.* (1985) 40, 51–61.



- Strausz, O.P. Bitumen and heavy oil chemistry, Chapter 3 in *AOSTRA technical handbook on oil sands, bitumens and heavy oils*, (1989) ed. L.G. Hepler and C. Hsi, Alberta Oil Sands Technology and Research Authority, Edmonton.
- Svrcek, W.Y., and Mehrotra, A.K. One parameter correlation for bitumen viscosity, *Chem. Eng. Res. Des.* (1988) 66, 323–327.
- Takamura, K. Microscopic structure of Athabasca oil sand, *Can. J. Chem. Eng.* (1982) 60, 538–545.
- Takamura, K. Physico-chemical characterization of Athabasca oil sand and its significance to bitumen recovery, *AOSTRA J. Research* (1985) 2, 1–10.
- Takamura, K., and Chow, R.S. A mechanism for initiation of bitumen displacement from oil sand, *J. Can. Petrol. Technol.* (1983, November–December) 22, 1–9.
- Takamura, K., and Isaacs, E.E. Interfacial properties, Chapter 5 in *AOSTRA technical handbook on oil sands, bitumens and heavy oils*, (1989) ed. L.G. Hepler and C. Hsi, Alberta Oil Sands Technology and Research Authority, Edmonton.
- The Petroleum Resources Communication Foundation, *Our petroleum challenge: the new era*, 2nd edition (1980) Calgary.
- Thompson, G.R. Evaluation of a microwave-NMR method for oil sand oil-water-solids analysis, *AOSTRA J. Research* (1989) 5, 135–143.
- Trevoy, L.W., Schutte, R., and Goforth, R.R. Development of the heavy minerals potential of the Athabasca tar sands, *Can. Mining and Metall. Bull.* (1978) 71, 175–180.
- Tyerman, W.J.R. Interaction of surfactants with dispersions of bitumen-solvent-solids-water, *AOSTRA J. Research* (1989) 5, 183–189.
- Vorndran, L.D.V., Serres, A.J., Donnelly, J.K., Moore, R.G., and Bennion, D.W. Bitumen separation for experimental use, *Can. J. Chem. Eng.* (1980) 58, 580–587.
- Wallace, D., and Kratochvil, B. Sampling uncertainty in the determination of major components in Athabasca oil sand, *AOSTRA J. Research* (1984a) 1, 31–35.

- Wallace, D., Kratochvil, B., and Jo, D.L. Effects of sampling and analytical uncertainty on the determination of bitumen variability in oil sand as measured by sulphur content, *AOSTRA J. Research* (1984b) 1, 83–87.
- Wallace, D., Polikar, M., and Ferracuti, F. Preparation of bitumen from oil sand by centrifugation, *Fuel* (1984c) 63, 862–864.
- Wallace, D., and Kratochvil, B. Evaluation of statistical sampling methods for Athabasca oil sand, *AOSTRA J. Research* (1986) 2, 233–239.
- Wallace, D., and Henry, D. A correlation for correcting the viscosity of solvent-extracted bitumen to a solvent-free basis, *AOSTRA J. Research* (1987) 3, 239–248.
- Wallace, D., Starr, J., Thomas, K.P., and Dorrence, S.M. Characterization of oil sand resources, (1988) Alberta Oil Sands Technology and Research Authority, Edmonton.
- Wallace, D. (ed.), A review of analytical methods for bitumens and heavy oils, (1988) Alberta Oil Sands Technology and Research Authority, Edmonton.
- Wightman, D., Rottenfusser, B., Kramers, J., and Harrison, R. Geology of the Alberta oil sands deposits, Chapter 1 in *AOSTRA technical handbook on oil sands, bitumens and heavy oils*, (1989) ed. L. G. Hepler and C. Hsi, Alberta Oil Sands Technology and Research Authority, Edmonton.
- Williams, P.J., and Duchowski, J. A technique for rapid separation of tar sands, *American Laboratory* (1983, August) 78–83.
- Wood, P., and Hepler, L.G. Unpublished research at University of Alberta and Syncrude.
- Yang, Y.J., Bukka, K., and Miller, J.D. Selection and evaluation of diluents in the modified hot water process, *Energy Processing/Canada* (1989, September–October) 14–21.
- Xu, Y., and Hepler, L.G. Henry's law constants and thermodynamic properties of gases and vapours in bitumens, *Can. J. Chem. Eng.* (1990) 68, 1024–1032.

# 2

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## *Separation of Bitumen from Mined Oil Sands*



## **INTRODUCTION**

The "fundamentals" research program that is being described in this book was intended to contribute to kinds of improved or extended scientific understanding that can provide part of the foundation for development of improvements in the hot water process for separating bitumen from mined oil sands. Examples of kinds of improvements that might be made include the following:

- (i) Improved recovery from low grade ores or other ores that are presently difficult to process;
- (ii) Recovery of better quality froth (lower solids content and/or less water);
- (iii) Process modifications that will lower the operating cost or capital costs;
- (iv) Process modifications that will diminish "external" problems such as those involving tailings disposal, recycle water, and make-up water.

As background information, in the next two sections we provide a description and schematic illustration of the hot water separation process that is presently used, followed by brief descriptions of some other separation processes that have been proposed.

## **THE HOT WATER PROCESS**

The hot water process for separating bitumen from mined oil sands has been described in many publications. We call attention to the following publications that provide useful summaries or illustrations and also specific information about the hot water process: Allen (1974), Bowman (1969), Camp (1976ab), McRory (1982), Erskine (1984), and Ferguson (1985). Other references that are more directly related to the research described in this book are the following: Schramm and Smith (1984), Smith and Schramm (1984), Schramm and Smith (1989), and Smith and Schramm (1989).

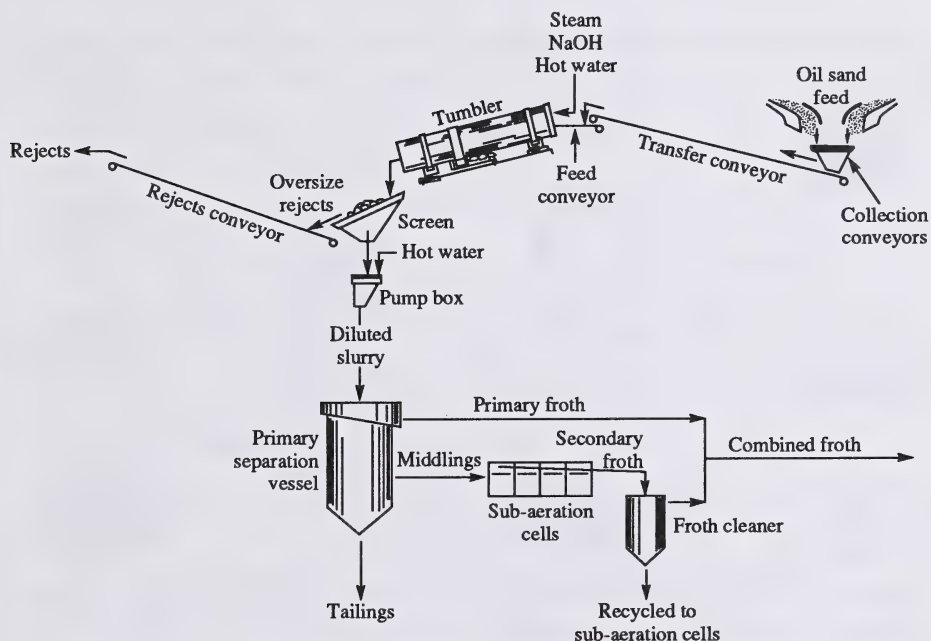
The separation part of the integrated mining, separation, and upgrading process can be summarized (based on references cited above) in terms of the following operations.



The mined oil sands are “conditioned” by slurrying with hot water (partly or entirely recycled water from the tailings pond), low quality steam, and sodium hydroxide in a rotating drum that is called the conditioning drum or the tumbler. After residence time of 2–3 minutes, the slurry is screened to remove over-size material such as rocks and lumps of clay. The next step is dilution of the slurry with more hot water (also partly or entirely recycled pond water), with the diluted or “flooded” slurry going to the primary separation vessel. In the primary separation vessel, much of the bitumen floats and is removed as primary froth. Much of the sand (with some other minerals and a little bitumen) sinks and is removed as primary tailings. The “middlings” (below the primary froth, above the primary tailings), which contain water, bitumen, and fine minerals (mostly clays), are withdrawn from the primary separation vessel and sent to the secondary recovery circuit where still more bitumen is recovered in the secondary froth that is produced by forced air flotation. The primary froth and the secondary froth are combined and naphtha is added as diluent. This combined and diluted froth is sent to centrifuges where the diluted bitumen is separated from water and suspended fine minerals. Figure 2.1 is a schematic illustration of this sequence of operations in the commercial hot water process and Figure 2.2 illustrates a laboratory-scale extraction apparatus that has been found to yield results that correlate well with recovery of bitumen in the commercial process.

Various specifics (temperature, water/oil sand ratios, amounts of NaOH, etc.) of the hot water process as applied in recent years are summarized in Table 2.1. Note that the quantities listed in Table 2.1 are illustrative rather than exact; various publications (1976–1989) cited earlier have listed somewhat different amounts, ratios, etc. The different values that have been reported are not mistakes, but reflect changes in operation that have resulted from changes in feed stock and improvements in the process over a period of several years. Therefore, the quantities listed in Table 2.1 are intended to provide some sort of “average picture” of conditions for carrying out the hot water separation process.

Kessick (1982,1983abc) has described an “alkali recycle” scheme involving lime addition that results in substantial recovery of the sodium hydroxide that is usually added in the early stages of the hot water process for recovering bitumen from mined oil sands. A variation of this alkali recycle scheme also has potential

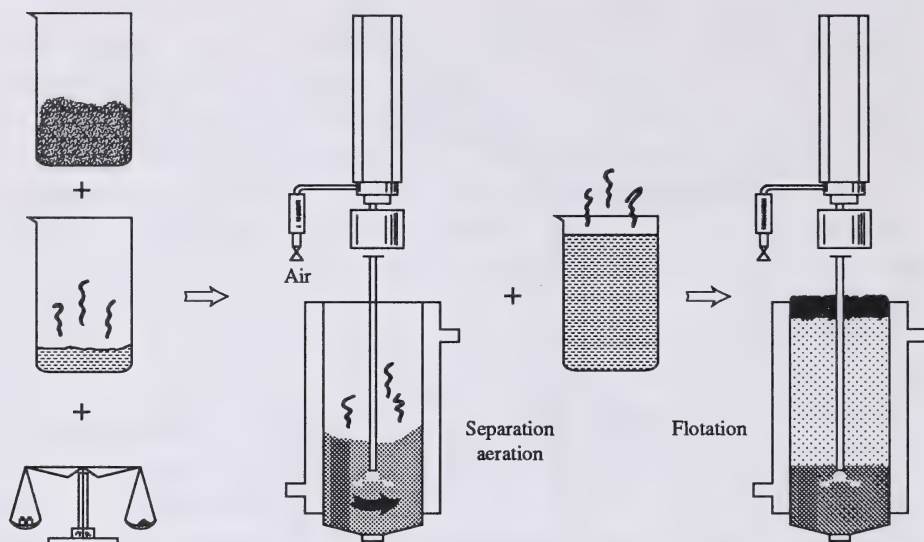


**Figure 2.1.** Schematic illustration of Syncrude's hot water process for separating bitumen from mined oil sands.

applications in the treatment of tailings sludge, as summarized by Kasperski (1992). Research in this area is continuing at Syncrude.

## SOME OTHER PROCESSES FOR SEPARATING BITUMEN FROM MINED OIL SANDS

In this section we will discuss briefly several other (different than the hot water process) processes for the separation of bitumen from mined oil sands. Our attention here is focussed on those separation processes that use one or more liquids because all liquid-based processes have something in common with the hot water process that is our principal present interest.



**Figure 2.2.** Schematic illustration of Syncrude's batch extraction unit for laboratory investigation of separation of bitumen from mined oil sands.

It has been recognized for a long time that there *might* be advantages (lower cost, better product quality, easier-to-manage tailings, etc.) to be obtained by modifying the hot (about 80°C) water process to operate at some lower temperature.

Factors to be considered in evaluating and possibly implementing any lower temperature modification of the hot water process include the following. First, the saving in cost of thermal energy may not be of much importance because of the possible availability of low cost (otherwise not used) thermal energy from other parts of the integrated process that includes upgrading. On the other hand, the saving in energy can be important for a separation process that takes place in a location that is remote from the upgrading plant. There is also the possibility that the present upgrading process will be replaced by some other process (asphaltenes removal or ???) that does not yield energy to be used elsewhere.

In general, it is to be expected that there will be operating difficulties with low temperature processes, related to the fact that the viscosity of bitumen increases

**Table 2.1.** *Some illustrative operating conditions for the hot water process for separating bitumen from mined oil sands*

- 
- Temperature in the conditioning drum/tumbler:  $\approx 80^{\circ}\text{C}$ .
  - (Mass water/mass oil sand) in tumbler: 1/4.
  - Amounts of NaOH usually used in the batch extraction unit, pilot plant, or Syncrude commercial plant:
    - Medium grade feed (10–11% bitumen): 0.01 to 0.04 wt% NaOH;
    - Low grade feed (6–9% bitumen): 0.02 to 0.08 wt% NaOH;
    - These wt% values are based on mass of oil sand; hence medium grade oil sand is treated with 0.1 to 0.4 g of NaOH per kg of oil sand and low grade oil sand is treated with 0.2 to 0.8 g of NaOH per kg of oil sand. This NaOH is usually added as a 20% aqueous solution.
  - Residence time in tumbler: 2–3 minutes.
  - (Mass water/mass oil sand) in diluted or flooded slurry: 0.7/1.
  - Temperature in primary separation vessel:  $70\text{--}75^{\circ}\text{C}$ .
  - Typical primary recovery: 85–90% of bitumen in original feedstock.  
 Typical primary froth composition:   60–65% bitumen  
   6–7% fine solids  
   28–34% water.
  - Temperature in secondary recovery vessel:  $75^{\circ}\text{C}$ .
  - Typical secondary recovery: 5–10% of bitumen in original feedstock.
- 

considerably with decreasing temperature; it is partly for this reason that solvent or diluent-assisted processes have been considered, as discussed later in this chapter

Smith and others at Syncrude have operated the laboratory-scale batch extraction unit at temperatures as low as  $50^{\circ}\text{C}$ , with good recoveries of bitumen. They have found that successful operation at temperatures lower than about  $80^{\circ}\text{C}$  requires longer times for conditioning; that is, the typical conditioning time required for good recovery is three or four times as long at  $50^{\circ}$  as at  $80^{\circ}\text{C}$ . For temperatures below about  $50^{\circ}\text{C}$ , these researchers obtained poor recoveries of bitumen even with very long residence times in the conditioning tumbler.



Finally, it should be recognized that operating costs for the separation process are only a small part (about 12%) of *total* operating costs, so *small* decreases or increases in cost of separation may not have as much overall importance as do such factors as percentage recovery of bitumen, product quality, and impact on tailings.

Utah "tar" sands differ from Athabasca "oil" sands ("bituminous" sands might be the best label for both) in several respects. One important difference is that the Utah tar sands typically contain less than 0.5 wt% water (distinctly less water than in Athabasca oil sands). As might be expected from the low water content, most of the minerals in Utah tar sand appear to be in direct contact with bitumen, rather than separated from the bitumen by a layer of water as in the Athabasca oil sands. Another difference is that most Utah bitumen is more viscous than most Athabasca bitumen. In spite of these important differences, there are enough similarities to justify consideration of research done on Utah tar sands as a source of potentially useful information for us. In particular, we call attention to a recent paper by Misra and Miller (1991), who have compared various water-based separation processes for Utah tar sands. We also call attention to other papers from researchers in Utah as follows: Sepulveda and Miller (1978); Misra and Miller (1980); Smith and Miller (1981); Miller and Misra (1982); Misra et al. (1981); Hupka et al. (1984); Hupka et al. (1987); Oblad et al. (1987); Yang et al. (1989); Hupka and Miller (1991ab); Hupka et al. (1991); Bukka et al. (1991); and Hupka and Miller (1992).

Now we turn to brief summaries of several possible alternatives to the hot water processes for separating bitumen from mined oil sands.

### **Sand Reduction Process**

Extensive investigations of a cold water process were carried out by J.A. Bichard, C.W. Bowman, R.M. Butler, and J.L. Tiedje, each of whom has made important contributions to production of bitumen and thence synthetic crude from Alberta's oil sands. Their "sand reduction process" has been described in the Bichard book (1987) and by Bichard et al. (1963). Three quotations from Bichard et al. (1963) provide reasons for development of the process and identify some attractive features of the process.



"... In the present study an attempt has been made to devise a simple process for removing enough sand to make direct distillation and coking economically attractive. This contrasts with the usual separation approach where the objectives are to recover the maximum amount of oil with minimum contamination of the product by solids and water."

"A process of sand reduction reduces the solids content of the Athabasca oil sand to the extent where direct distillation and coking in a fluidized-solids bed may be economically practical. In this process, oil sand is mixed with water at low temperatures, clean sand separates, and the oil particles released from the structure agglomerate to form an oil phase. The agglomerate is then separated from the solids. The enriched-oil phase is processed directly, and water is recycled to the process."

"The results of studies in small-scale laboratory apparatus and pilot-plant equipment on sand reduction have indicated that this process has the following attractive features: (1) low operating temperature, (2) good oil-recoveries, (3) tolerance to clay and silt in feed and in recycle water, (4) relatively dry oil-phase, hence less heat requirement in direct distillation and coking, (5) no solvent required, (6) no sludge produced."

The sand reduction process proposed by Richard et al. can be described briefly as follows.

Mined oil sands are mixed with water in apparatus such as a trough mixer, kneader, or pug mill. After mixing, much of the sand passes through a screen, which retains relatively large agglomerates of bitumen + minerals. These agglomerates constitute the "sand-reduced" material that is intended to be more suitable than the original oil sands for direct coking or other upgrading process.

After small scale bench testing, Richard et al. designed and built a continuous flow demonstration pilot plant in which oil sands and water were fed to a hopper and then to a helix mixer or to a pug mill. The resulting mixture was fed to a submerged rotating screen, which separated clean sand from the bitumen-containing agglomerates.

Typical sand reduction experiments involved mixing mined oil sand with water in amounts corresponding to weight ratios of (water/oil sand) ranging from 0.6 to 1.1 at about 70°F (23°C). The process then led to removal of 60 to 80 wt% of the sand, with bitumen losses ranging from nearly zero to as high as about 40%. In

general, smaller per cent sand reductions and larger losses of bitumen were obtained with lower grade oil sands or oil sands that were "aged" (exposed to air for some time after being mined). It was observed that blending low grade oil sands with higher grade oil sands led to sand reductions and bitumen recoveries that were characteristic of the good results obtained separately with medium and high grade oil sands.

Results of some more recent investigations of a sand reduction process have been reported by McKay and Phillips (1981), who focussed on use of a plate mill with cold water as a means of determining the dependence of sand reduction and bitumen recovery on such factors as Reynolds number, ratio of oil sands to water, and dimensions of the mixing mill.

McKay and Phillips have suggested that the bitumen content in the separated agglomerates appears to approach a limit of about 27 mass per cent. We note, however, that the pilot plant results of Bichard et al. led to agglomerates containing from about 17% to about 40% bitumen. Because of differences between the mixing processes and the feed stocks used by McKay and Phillips and by Bichard et al., no great significance should be attached to differences in the specific compositions reported by each group. But it is clear that the sand reduction process does lead to agglomerates that contain substantially larger percentages of bitumen and correspondingly smaller percentages of minerals than did the original oil sand.

The original motive for investigating the sand reduction process was to obtain material that would be better suited than mined oil sands for use as feed stock for the fluidized bed direct distillation and coking process developed by Peterson and Gishler (1951). It is now possible that the sand reduction process can be used in combination with the more recently developed Taciuk direct thermal processor as described by Taciuk (1984) and by Turner et al. (1989).

As background for the following discussion of the spherical agglomeration process, it is interesting to note that Bichard et al. observed that the bitumen-rich agglomerates resulting from their sand reduction process were roughly spherical in shape.

## **Spherical Agglomeration**

The spherical agglomeration method that has been developed by Puddington, Capes, Sparks, Meadus, and others at the National Research Council of Canada and also applied to oil sands is closely related to the sand reduction process described in the preceding section. The NRC agglomeration technique can be considered to be a cold water process without added solvent as described by Sparks et al. (1971) or a solvent-assisted cold water process as described by Sparks and Meadus (1979,1981) and by Meadus et al. (1982ab). This latter process is sometimes called the SESA (for Solvent Extraction Spherical Agglomeration) process. Several solvents have been tested, including naphtha derived from bitumen. Because their agglomeration process works well with feed containing relatively large amounts of fines, it has been suggested that this method can be applied to high fines oil sands in ways that might (as compared with the hot water process) increase recovery of bitumen and decrease the accumulation of tailings sludge.

The spherical agglomeration or SESA process has been described concisely by Sparks and Meadus (1981) as follows. "Spherical agglomeration is a technique in which fine particles, in liquid suspension, can be formed into large, dense agglomerates of considerable integrity by preferential wetting with a second immiscible liquid, under appropriate agitation conditions. The naturally water wet conditions of the oil-sand grains make this system suitable for application of this technology as a means of achieving an improved separation of the solvent and the mineral phases, after solvent extraction of the bitumen component. In this case, the bitumen solution is utilized as the suspending medium and water is used as the immiscible second liquid to agglomerate the sand fraction. The result is a relatively clean bitumen solution and an agglomerated sand tailings with low solvent content. ... Because of comparatively high solvent costs the most important factor in this application of spherical agglomeration is the amount of residual solvent remaining with the agglomerated sand."

Hoefele et al. (1985) have reported results of semi-continuous bench-scale pilot plant tests of application of the SESA process (using naphtha as solvent) to mined Athabasca oil sands of three different grades (6.7 to 10.7% bitumen). Recoveries of 92 to 97% of the in-place bitumen were achieved. Residual naphtha in the tailings stream was less than 1000 ppm after steam stripping.

### Solvent-Assisted Cold Water Processes

Djingheuzian (1951) and Djingheuzian and Warren (1951) have described research at the Mines Branch in Ottawa on a solvent-assisted cold water method for separating bitumen from mined Athabasca oil sands. The essence of their cold water process is illustrated by the following quotation from Djingheuzian (1951): "When a light oil having the properties of kerosene is added to the bituminous sand at the same time as the bitumen films around the sand particles are ruptured or scoured off by some rubbing action, bitumen dissolves in the light oil, forming a compound oil with a specific gravity of less than one. When this process takes place in water, the heavier-than-water sand particles, liberated from oil, fall to the bottom of the vessel and the lighter oil rises to the surface. Thus, fundamentally, the cold-water process is a gravity concentration process in which the valuable constituent of the ore rises to the surface and the gangue sinks to the bottom."

Although the statement quoted above refers to "bitumen films around the sand particles," Djingheuzian was aware of Clark's earlier work on films or layers of water in oil sands, as illustrated by one of his remarks during the Discussion: "In bituminous sands, Dr. Clark's investigations disclosed that a very thin layer of water surrounds each sand particle and this in turn is surrounded by a bitumen film."

Further information about this early work on a cold water process is as follows.

It was shown that either kerosene or a distillate from Bitumount bitumen worked well as solvent-diluent. Other additives were a wetting agent (such as Span 40) and soda ash. It was noted that the amounts of clays had an effect on recovery of bitumen, similar to such effects observed by Clark and others in their work on the hot water process. Temperatures in the Djingheuzian-Warren cold water process were in the range 70–83°F (21–28°C).

Publications from the University of Utah as cited earlier in this chapter describe their investigations of solvent-assisted separation processes, in which a principal function of the solvent or diluent is to reduce the viscosity of the bitumen.



### **The Sury Low Temperature Froth Flotation Process**

Sury (1990) has patented a cold water process in which mined oil sands are treated with 100–800 ppm of a “conditioning agent” or “flotation agent” or “collector” (such as kerosene) and 50–400 ppm of a “frothing agent” or “frother” (such as methyl-isobutyl-carbinol) at temperatures ranging from 0–35°C, but preferably in the range 2–15°C. It was observed that the amount of mechanical shear energy input needed for good recovery depended on temperature, with more mechanical energy required at the lower temperatures, as summarized by the following quotation from the patent: “Thus mechanical shear and slurry temperature are interdependent and for an optimum recovery one may be exchanged for the other provided a minimum of each energy is maintained.” It is reported that recoveries of up to 96% of bitumen in the feed have been achieved, with froth consisting of 60–70% bitumen, about 20% solids, and 10–20% water. It is claimed that this process is applicable to oil sands that have been mined in several ways (conventional dry mining or various kinds of wet mining using water jets, etc.) and that the “fines problem” in tailings is much reduced as compared with the hot water process because this proposed new process does not require addition of sodium hydroxide, which leads to dispersion of the clay fines.

It should be emphasized that the Sury flotation process (bears a close resemblance to certain kinds of mineral processing by way of flotation) uses much smaller amounts of organic additives (“collector” plus “frother”) than do various solvent-assisted extraction processes discussed in the previous section or the solvent extraction processes discussed in the next section.

Although no detailed economic analysis of the Sury process has been published, it seems reasonable to expect that it will be a cheaper process than the hot water separation process used by Syncrude and Suncor, but will lead to increased upgrading costs due to the relatively large amounts of solids in the extracted bitumen.

### **Solvent Extraction Processes**

Alternatives to a cold water separation process that is assisted or improved by use of an organic solvent-diluent or a “collector” plus “frother” are solvent extraction processes that do not involve the use of any added water. Brief accounts of some such processes are as follows.



Early research at Cities Service Athabasca Inc. on a solvent extraction process has been described by Cottrell (1963). The proposed Cities Service process was described concisely by Cottrell as follows: "An anhydrous process for oil-sand extraction would as presently conceived result in a commercial plant in which a slurry of oil and sand plus hydrocarbon solvent would be placed on a moving belt passing over three drain chambers and a solvent-recovery chamber. The produced oil would go to a fractionation tower for solvent recovery and the raw bitumen to refining from which make-up solvent would be realized." A typical temperature of test experiments leading to their separation process was about 100°F (38°C).

It was reported (Cottrell, 1963) that the Cities Service process recovered more than 90% of the bitumen and that overall solvent recovery was satisfactory. Details of grades of oil sands tested, effects of fines on the process, loss of solvent to tailings, and fines entrapment in produced bitumen were not reported, nor was the "hydrocarbon" solvent identified in any specific way

Cormack et al. (1977) have carried out a systematic investigation of several aspects of solvent extraction of bitumen from mined Athabasca oil sands. Their investigations led to identification of solvent type, solids concentration, stirrer speed, and contact time as important parameters. It was concluded that aromatic solvents such as benzene and toluene are distinctly better in terms of total extraction and rate of extraction of bitumen than largely aliphatic solvents such as kerosene.

Dravo Corporation and Texas Gas Resources Corporation undertook design and operation of a pilot plant for solvent extraction of bitumen from oil sands mined in Kentucky, as reported by Tis et al. (1984). Their process involved percolation of a hydrocarbon solvent (confidential composition) through a stationary bed of mined (crushed) oil sand ore at some unspecified temperature. It was reported that residual bitumen on spent sand was often less than 0.3% of the original in-place bitumen. Solvent was recovered from spent sand by steam stripping. Although not explicitly stated, it was implied that the steam-stripped sand was suitable for disposal in the mine site.

Another solvent extraction process, investigated at Dow Chemical Company, makes use of methylene chloride ( $\text{H}_2\text{CCl}_2$ ) as solvent, as described by Gimber et al. (1985). This solvent has been selected for several reasons: (i) bitumen is very soluble in methylene chloride and the rate of solution is good; (ii) methylene chloride is

described as having low toxicity and no flash point; (iii) methylene chloride boils at a relatively low temperature and has low heat of vaporization, both of which contribute to efficient and economical recovery of solvent for recycle.

Gimber et al. (1985) have summarized the Dow solvent extraction process using methylene chloride as follows. "The overall process consists of a tumbler for mixing and extraction, a washer (or rinser) for sand-bitumen separation, a sand dryer for solvent recovery from the sand, a centrifuge for separation of the residual fine solids and a distillation system. This distillation system uses an intermediate boiling hydrocarbon to increase system vapor pressure, stripping residual solvent from the bitumen. The products of this process are dry sand for disposal, solvent-free bitumen and solvent for recycle use. The bitumen can contain some of the hydrocarbon chaser as a diluent to improve pumpability."

Herter and Herter (1984) and Babcock et al. (1985) have described their solvent extraction process that uses fatty acids (such as oleic acid) as solvent. After the fatty acid-oil phase is separated from the mineral matter, the fatty acid-oil phase is treated with aqueous sodium hydroxide, which extracts the anion of the fatty acid into the water phase. Subsequent addition of acid (such as HCl) converts the anion back to the fatty acid to be used again as extraction solvent. This use of relatively large amounts of fatty acids (also considered to be surfactants) as solvent is distinctly different than the hot water process that involves the presence of low concentrations of surfactants, as reported by Smith and Schramm in several papers and patents that are cited later in this book.

Ulrich et al. (1991) have provided a brief review of several solvent extraction processes as background for their investigations of the rate of dissolution of bitumen (from Spring Creek, Alabama, USA) into various solvents. Results of their work show that viscosity of the solvent and viscosities of solvent + bitumen mixtures that occur after some bitumen has dissolved are especially important in determining rates of dissolution. Ulrich et al. (1991) have also called attention to potentially useful earlier work by Farcasiu and Whitehurst (1977) on the use of mixed solvents, such as methanol + naphtha.

In general, it appears that some combination of the expenses of solvent recovery processes in combination with the costs of lost solvent (much more valuable than raw bitumen) make solvent extraction processes uneconomic in relation to the

hot water process. It should be recognized, however, that this general economic assessment is not necessarily applicable to the Sury process, which uses much smaller amounts of expensive solvent.

### **Oleophilic Sieve Method**

Kruger (1980,1982a,b,c,1983,1988) has described and patented use of the "oleophilic sieve" for recovery of bitumen from mined oil sands, while Thacker et al. (1985) have reported on a similar application to treatment of oil sands tailings.

### **Advantages and Disadvantages of Different Separation Processes**

It has been recognized since the early work of Clark, Pasternack, Bichard, and others that the separation process should not be considered entirely separately from the mining process, upgrading, and environmental problems. For example, a relatively inexpensive separation process that leads to bitumen containing large amounts of solids leads to a relatively expensive upgrading process; it is the sum of these costs that is important, rather than just the cost of either process taken separately. Similarly, there might be good economic justification for a relatively expensive separation process that leads to reduced costs to be associated with tailings and/or upgrading.

In Chapter 8 we return to further discussion of advantages and disadvantages of various separation processes, including their relationships to upgrading and tailings.

### **LABORATORY METHODS FOR INVESTIGATING RECOVERY OF BITUMEN FROM MINED OIL SANDS**

Because there are many variations in the properties of oil sands mined from different locations and depths and because there are many possible variations in the recovery process, it is desirable to have relatively simple methods for investigating many of these variables. In general, it can be expected that the simplest methods will yield the least detailed and least reliable information *per experiment*, but permit many investigations in a relatively short time and for relatively low cost. At the other

extreme, pilot plant tests are likely to provide the most detailed and most reliable information, all at larger cost for a smaller number of experiments.

Here we will focus on two laboratory methods: (i) the crumble test that was developed at the Alberta Research Council, and (ii) the batch extraction unit (sometimes informally called the "hot pot," and now often abbreviated to BEU) that was developed at Syncrude.

### **Crumble Test**

The crumble test that was developed and described by Currie et al. (1980) at the Alberta Research Council was intended originally to be an inexpensive method for investigating the relative effectiveness of aqueous surfactants for breaking up the oil sand matrix, but can be extended to investigations of effects of other additives to water and related effects of concentration of additive and pH. It is also possible to investigate effects of temperature of the extracting medium and effects of surface oxidation and dehydration associated with aging of mined oil sands.

The original procedure of Currie et al. (1980) is summarized by the following quotations:

"The procedure currently used to prepare pellets for testing was as follows: A chunk of oil sand (ca 200 g) was removed from the container and kneaded by hand in a polyethylene bag. Large pieces of rock and visible clay material were discarded to obtain more reproducible samples. Portions of 2.5 g of 'homogenized' oil sand were then compressed into a cylindrical shape (18 mm diameter and 7 mm thick) using an Instron press (Model TTC). A thin film of polyethylene was placed between the stainless steel die and the oil sand to prevent the pellet from sticking to the metal surface. Pressure was applied at 1.4 MPa (200 psig) for 10 minutes. After compression, each pellet was placed in a tightly capped vial and kept for 15 h at room temperature before refrigeration at 4°C. Prior to a run, a pellet was removed, left at room temperature for 1 h, and then the polyethylene film was carefully detached from the top and bottom surfaces."

"A run consisted of placing the pellet on a stainless steel mesh screen pan (mesh size 2 mm) attached to a recording electrobalance (Cahn, Model R-100). The



pan with the pellet was then submerged in an aqueous surfactant mixture; the subsequent weight change versus time as the pellet disintegrated and fell through the opening of the wire mesh pan was continuously recorded. Each pellet was allowed to crumble to 50% of its original weight. Constant temperature ( $\pm 0.5^\circ$ ) during a run was maintained by placing the vessel containing the aqueous surfactant phase in an external temperature controlled bath."

More recently, Doucet and Neale (1986) have carried out a systematic investigation of effects of such variables as various procedures for forming the pellet, mass of pellet, shape of pellet, etc.

### **Batch Extraction Unit (BEU)**

As a prelude to their description of the Syncrude batch extraction unit for investigating the separation of bitumen from mined oil sands, Sanford and Seyer (1979) provided references and brief accounts of earlier efforts to investigate what they have called "processibility". A general goal of all of these efforts was to obtain information about the effects of process variables (input of mechanical energy, added NaOH and possibly other chemicals, presence of fine minerals, temperature, etc.) and also to yield laboratory results that would correlate well with pilot plant and commercial production plant operations. These earlier small scale laboratory investigations did yield sufficient information to form the basis for subsequent pilot plant operations and design of two successful commercial production plants, but were inadequate in other ways mentioned by Sanford and Seyer.

The objectives behind design of the Syncrude batch extraction unit have been summarized by Sanford and Seyer (1979) as follows.

"In order to carry out detailed studies of the chemical and physical properties of tar sand as they affect processibility, it is necessary to have an extraction unit which (a) gives reproducible yield data, (b) is sensitive to changes in conditions so that additives, etc., can be evaluated and (c) is versatile so that temperature, stirring rates, etc., can be easily changed. In addition, it is desirable that the unit be designed or operated in such a way that trends established on the laboratory unit can be used to predict trends on larger pilot-scale units."



Figure 2.2 provides an illustration of the Syncrude batch extraction unit, which was designed to work with 500 g samples of oil sand. The extraction cell is jacketed to permit control of temperature. A stirrer (variable speed, different sizes and shapes of impeller can be used) mixes oil sand with water and introduces mechanical energy. Air is added through the stirrer shaft, which permits simulation of the secondary recovery step of the commercial extraction process.

Sanford and Seyer (1979) provided directions for operating their batch extraction unit and for analysis of tar sand samples, froth, middlings, and tailings. More detailed descriptions of analytical procedures have been provided in the Syncrude book of analytical methods prepared and edited by Bulmer and Starr (1979) and in other publications that have been cited in Chapter 1. In addition, Smith (see Appendix 3) has prepared a detailed step-by-step account of his procedure for operating the batch extraction unit and for some related analyses.

Sanford and Seyer (1979) used their batch extraction unit for several investigations, with a principal focus on the effect of added caustic (NaOH) on recovery of bitumen. One important result of their investigations was demonstration of the role of surfactants (derived by reaction of NaOH with acidic constituents of bitumen) in the separation process. Several references cited elsewhere in this book are primarily concerned with further investigations of the role of these "natural" surfactants in the separation process; many of these investigations made use of the batch extraction unit, which has proven to be one of the most useful methods for investigating mined oil sands.

## REFERENCES

- Allen, A.R. The mining and extraction of bitumen from the Athabasca tar sands, *CIM Bull.* (1974, June) 97-108.
- Babcock, R.E., Daniel, R.D., and Herter, G.L. The Herter solvent extraction process for the recovery of heavy oils and tars, in *The third UNITAR/UNDP international conference on heavy crude and tar sands*, (1985) pp. 732-737, ed. R. F. Meyer, Alberta Oil Sands Technology and Research Authority, Edmonton.

- Bichard, J.A. *Oil sands composition and behavior research: the research papers of John A. Bichard, 1957-65*, (1987) Alberta Oil Sands Technology and Research Authority, Edmonton.
- Bichard, J.A., Bowman, C.W., Butler, R.M., and Tiedje, J.L. Separation of oil from the Athabasca oil sands by sand reduction, in *The K.A. Clark volume*, (1963) ed. M.A. Carrigy, Information Series No. 45, Research Council of Alberta, Edmonton.
- Bowman, C.W. Mining the Athabasca tar sands, *Science Journal* (1969, November) 5A, 28-33.
- Bukka, K., Miller, J.D., Hanson, F.V., and Oblad, A.G. Mineral matter distribution during the hot water processing of Utah tar sand, *AOSTRA J. Research* (1991) 7, 101-109.
- Bulmer, J.T., and Starr, J. eds., *Syncrude analytical methods for oil sand and bitumen processing*, (1979) Syncrude Canada Ltd., Edmonton.
- Camp, F.W. *The tar sands of Alberta, Canada*, 3rd ed., (1976a) Cameron Engineers, Inc., Denver.
- Camp, F.W. Processing Athabasca tar sands-tailings disposal, (1976b) in *Symposium on tar sands*, 26th Canadian Chemical Engineering Conference, Toronto.
- Cormack, D.E., Kenchington, J.M., Phillips, C.R., and Leblanc, P.J. Parameters and mechanisms in the solvent extraction of mined Athabasca oil sand, *Can. J. Chem. Eng.* (1977) 55, 572-580.
- Cottrell, J.H. Development of an anhydrous process for oil-sand extraction, in *The K.A. Clark volume*, (1963) ed. M.A. Carrigy, Information Series No. 45, Research Council of Alberta, Edmonton.
- Currie, D.J., Hathaway, A.P., Isaacs, E.E., Mar, A., Morrison, D.N., and Richmond, C. The potential of the crumble test as a tool for tar sands research, Preprint for *Proceedings of the 30th Canadian chemical engineering conference, Volume IV: Oil sands, coal and energy modelling*, (1980) pp. 1125-1142.

- Djingheuzian, L.E. Cold-water method of separation of bitumen from Alberta bituminous sand, in *Proceedings: Athabasca oil sands conference*, (1951) Government of Alberta, pp. 185–197, Edmonton.
- Djingheuzian, L.E., and Warren, T.E. A study of cold-water separation of bitumen from Alberta bituminous sand on a pilot-plant scale, *Can. J. Research* (1951) 29, 170–189.
- Doucet, L., and Neale, G. Effects of oil-sand pellet preparation on crumble test behavior, *AOSTRA J. Research* (1986) 3 61–66.
- Erskine, H.L. Suncor hot water process, Chapter 5-1 in *Handbook of synfuels technology*, ed. R.A. Meyers, (1984) McGraw-Hill, New York.
- Farcasiu, M., and Whitehurst, D. Double solvent extraction of organic constituents from tar sands. (1977) U.S. Patent 4,046,668.
- Ferguson, B.G. *Athabasca oil sands: northern resource exploration 1875–1951*, (1985) Alberta Culture, Edmonton.
- Gimber, G., Groves, K., Haschke, M., Lastovica, J., and Rademacher, G. Oil sand processing using methylene chloride, in *Challenges and innovations: heavy oil & oil sands technical symposium* (1985, February), University of Calgary.
- Herter, G.L., and Herter, C. Recycle fatty acid crude petroleum recovery processes, (1984) U.S. Patent 4,480,691.
- Hoefele, E.O., Hamilton, J.F., and Filby, J.E. Processing of Athabasca oil sands by agglomeration and solvent extraction, in *The third UNITAR/UNDP international conference on heavy crude and tar sands*, (1985) pp. 751–760, ed. R.F. Meyer, Alberta Oil Sands Technology and Research Authority, Edmonton.
- Hupka, J., Oblad, A.G., and J.D. Miller. Hot water processing of U.S. tar sands-water recycle and tailings disposal, *Stud. Environ. Sci.* (1984) 23, 253–267.
- Hupka, J., Oblad, A.G., and Miller, J.D. Diluent-assisted hot-water processing of tar sands, *AOSTRA J. Research* (1987) 95–102.

- Hupka, J., and Miller, J.D. Electrophoretic characterization and processing of Asphalt Ridge and Sunnyside tar sands, *Int. J. Mineral Processing* (1991a) 31, 217–231.
- Hupka, J., and Miller, J.D. Moderate-temperature water-based bitumen recovery from tar sand, *Fuel* (1991b) 70, 1308–1312.
- Hupka, J., Drelich, J., Miller, J.D., White, R.R., Hanson, F.V., and Oblad, A.G. Impact of water recycle on water-based processing of Whiterocks tar sand, *Fuel* (1991) 70, 1313–1315.
- Hupka, J., and Miller, J.D. Tar sand pretreatment with diluent, Preprint, SME Annual Meeting (1992, February) Phoenix, Arizona.
- Kasperski, K.L. A review of properties and treatment of oil sands tailings, *AOSTRA J. Research* (1992) 8, 11–53.
- Kessick, M.A. Alkali recycle process for recovery of heavy oils and bitumens, (1982) Canadian Patent 1,129,801.
- Kessick, M.A. Recovery of water and alkali used in oil sands and heavy oil extraction, *Fuel* (1983a) 62, 1296–1298.
- Kessick, M.A. Alkali recycle process for recovery of heavy oils and bitumens, (1983b) U.S. Patent 4,392,944.
- Kessick, M.A. Alkali recycle process for recovery of heavy oils and bitumens, (1983c) U.S. Patent 4,409,091.
- Kruyer, J. Process for recovering bitumen from tar sand, (1980) Canadian Patent 1,085,760.
- Kruyer, J. Process for recovering bitumen from tar sand, (1982a) Canadian Patent 1,129,363.
- Kruyer, J. Process for recovering bitumen from tar sand, (1982b) Canadian Patent 1,132,473. Also U.S. Patent 4,392,949.
- Kruyer, J. Oleophilic separation of tar sands, oil-water mixtures, and minerals, in *The future of heavy crude and tar sands*, 2nd international conference, (1982c) pp. 1087–1095, ed. R.F. Meyer, J.C. Wynn, and J.C. Olson, McGraw-Hill, New York.



- Kruyer, J. Preparation of bitumen froths and emulsions for separation, (1983) U.S. Patent 4,405,446. Also Canadian Patent 1,144,498.
- Kruyer, J. Reducing the sludge problem by co-processing sludge with oil sands ore, in *Proceedings: The fourth UNITAR/UNDP international conference on heavy crude and tar sands*, vol. 5 (1988) pp. 19–35, ed. R.F. Meyer and E.J. Wiggins, Alberta Oil Sands Technology and Research Authority, Edmonton.
- McKay, A.M., and Phillips, C.R. Fundamentals of mechanical upgrading of Athabasca oil sands: mechanisms of sand and bitumen separation, *Separation Sci. and Technol.* (1981) 16, 237–252.
- McRory, R.E. *Oil sands and heavy oils of Alberta*, (1982) Alberta Energy and Natural Resources, Edmonton.
- Meadus, F.W., Chevier, P.J., and Sparks, B.D. Solvent extraction of Athabasca oil sand in a rotating mill, part I: dissolution of bitumen, *Fuel Proc. Technol.* (1982a) 6, 277–287.
- Meadus, F.W., Bassaw, B.P., and Sparks, B.D. Solvent extraction of Athabasca oil sand in a rotating mill, part II: solids-liquid separation and bitumen quality, *Fuel Proc. Technol.* (1982b) 6, 289–300.
- Miller, J.D., and Misra, M. Concentration of Utah tar sands by an ambient temperature flotation process, *Int. J. Mineral Processing* (1982) 9, 269–287.
- Misra, M., Aguilar, R., and Miller, J.D. Surface chemistry features in the hot water processing of Utah tar sand, *Separation Sci. and Technol.* (1981) 16, 1523–1544.
- Misra, M., and Miller, J.D. The effect of feed source in the hot water processing of Utah tar sand, *Mining Eng.* (1980) 32, 302–311.
- Misra, M., and Miller, J.D. Comparison of water-based physical separation processes for U.S. tar sands, *Fuel Proc. Technol.* (1991) 27, 3–20.
- Oblad, A.G., Bunger, J.W., Hanson, F.V., Miller, J.D., Ritzma, H.R., and Seader, J.D. Tar sand research and development at the University of Utah, *Ann. Rev. Energy* (1987) 12, 283–356.



- Peterson, W.S., and Gischler, P.E. The fluidized solids technique applied to the Alberta oil sands problem, in *Proceedings: Athabasca oil sands conference*, (1951) Government of Alberta, pp. 207–236, Edmonton.
- Sanford, E.C., and Seyer, F.A. Processibility of Athabasca tar sand using a batch extraction unit: the role of NaOH, *CIM Bull.* (1979, March) 72, 164–169.
- Schramm, L.L., and Smith, R.G. Control of process aid used in hot water process for extraction of bitumen from tar sand, (1984) U.S. Patent 4,462,892.
- Schramm, L.L., and Smith, R.G. Some parametric studies of oil sand conditioning in the hot water flotation process, *AOSTRA J. Research* (1989) 5, 87–107.
- Sepulveda, J.E., and Miller, J.D. Separation of bitumen from Utah tar sands by a hot water digestion-flotation technique, *Mining Eng.* (1978) 30, 1311–1320.
- Smith, R.G., and Schramm, L.L. Blending tar sands to provide feedstocks for hot water process, (1984) U.S. Patent 4,474,616.
- Smith, R.G., and Schramm, L.L. Processibility of Athabasca oil sand by the hot-water process when contaminated with overburden material, *Fuel Proc. Techn.* (1989) 23, 215–231.
- Smith, R.J., and Miller, J.D. The flotation behavior of digested Asphalt Ridge tar sands, *Mining Eng.* (1981) 33, 1719–1724.
- Sparks, B.D., Meadus, R.W., and Puddington, I.E. The continuous separation of tar sands by oil-phase agglomeration, *CIM Trans.* (1971) 74, 169–174.
- Sparks, B.D., and Meadus, F.W. A combined solvent extraction and agglomeration technique for the recovery of bitumen from tar sands, *Energy Processing Canada* (1979, September–October) 1–6.
- Sparks, B.D., and Meadus, F.W. A study of some factors affecting solvent losses in the solvent extraction-spherical agglomeration of oil sands, *Fuel Proc. Technol.* (1981) 4, 251–264.
- Sury, K.N. Low temperature bitumen recovery process, (1990) U.S. Patent 4,946,597.

- Taciuk, W. Development status of the Taciuk direct thermal processor for oil sands and heavy oils, in *The future of heavy crude and tar sands*, 2nd International UNITAR Conference (1984), pp. 1096–1103, ed. R.F. Meyer, J.C. Wynn, and J.C. Olson, McGraw-Hill, New York.
- Thackrar, A.C., Kruyer, J., and Webster, I.C. Application of the oleophilic sieve to recovery of bitumen from tailings pond sludge, in *Advances in petroleum recovery & upgrading technology*, (1985) Alberta Oil Sands Technology and Research Authority, Edmonton.
- Tis, D.J., Culbertson, R.W., and Kelley, M.N. Recent developments with the Dravo solvent extraction process for tar sand, *Energy Progress* (1984, March) 4, 56–59.
- Turner, L.R., Wright, B.C., and Taciuk, W. Oil shale processing with the AOSTRA processor, in *Proceedings: The fourth UNITAR/UNDP international conference on heavy crude and tar sands*, vol. 5, pp. 439–447, ed. R.F. Meyer and E.J. Wiggins, Alberta Oil Sands Technology and Research Authority, Edmonton.
- Ulrich, R.K., Koppaiah, M.K., and Majmudar, V.K. Application of the rotating disk method to the study of bitumen dissolution into organic solvents. *Can. J. Chem. Eng.* (1991) 69, 825–832.
- Yang, Y.J., Bukka, K., and Miller, J.D. Selection and evaluation of diluents in the modified hot water process, *Energy Processing/Canada* (1989, September–October) 14–21.



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***Chemical Constituents of Oil Sands  
and their Roles in the Hot Water  
Separation Process***





## **INTRODUCTION**

It is convenient to make somewhat arbitrary classifications of properties of oil sands and individual components as "chemical" or "physical." It is also convenient to make similar arbitrary classifications of experimental methods. Examples of the arbitrariness and ambiguities in these classifications are mentioned briefly below, before we proceed with discussion of "chemical" properties and methods in this chapter, followed by related discussion of "physical" properties and methods in Chapter 4.

We know that some components of bitumen undergo chemical reactions with sodium hydroxide to produce chemical compounds that are surface-active (surfactants); we also know that these surfactants derived from bitumen are important in the hot water process for separating bitumen from mined oil sands. It is therefore appropriate to consider formation of these surfactants as an important chemical process. However, measurements of surface tension are a principal part of the detection and analysis procedure for surfactants derived from bitumen. Because surface tension is usually considered to be a physical (rather than chemical) property, we often think of so-called physical measurements in this connection.

As previously noted in Chapter 1 and as also discussed later in this book, properties of the minerals (especially the fine minerals, such as clays) have a very important influence on the extent of recovery of bitumen by way of the hot water process. These fine minerals affect the hot water process as a result of certain identifiable chemical reactions and also as a result of adsorption (due to both chemical and physical interactions of surfactants with the minerals). In addition, the fine minerals affect viscosity, as discussed in Chapter 4.

The examples mentioned above, and others that might be mentioned, illustrate that many of the properties that are important in processing mined oil sands and also the methods used to investigate these properties have both "chemical" and "physical" components, which means that our (or any other) classification scheme is partly arbitrary. Nevertheless, it has proven convenient to make such semi-arbitrary classifications and thence to discuss chemical problems and methods in this chapter, followed by discussion of physical methods and related properties in Chapter 4.

## **SURFACTANTS AND COMPLEXING CHEMICALS**

### **Clark and Pasternack**

Clark and other early investigators of the hot water process for separating bitumen from mined oil sands recognized in a general way that surface-active substances present in bitumen or derived from bitumen were important in the separation process. They also recognized that effects due to these surface-active substances were influenced by amounts of sodium hydroxide added, presence of fine minerals, and presence of compounds or ions of iron, calcium, etc. Results of many of these investigations and related conclusions about the hot water process have been summarized in reports by Clark and Pasternack (1949) and by Pasternack and Clark (1951). Many of the subsequent investigations to be discussed in this chapter can be regarded as following naturally from these early observations.

### **Bichard**

In the period 1957–1965, Bichard (1987) carried out many investigations of mined oil sands, leading toward industrial application of the hot water process for separating bitumen from mined oil sands. Several of Bichard's investigations and conclusions are directly relevant to our present discussion of surfactants and complexing or chelating agents.

Bichard observed that some components of bitumen were soluble in water, and also observed that the solubility was greater in acidic solutions and in alkaline solutions than in water with pH near 7. He recognized that this kind of effect of pH on solubility demonstrated that some components of the bitumen have acidic properties (react with hydroxide ions to yield soluble species) and basic properties (react with hydrogen ions to yield other soluble species). Bichard specifically described these water soluble substances as surfactants.

Bichard wrote "As naturally occurring surfactants have been found to be an important factor in the Hot Water Flotation Process, it is logical to evaluate the addition of other organic compounds . . . for effects and enhancements. Further, as polyvalent ions are bridging agents in solids/bitumen association, organic compounds that complex or sequester these ions were preferentially selected in these

preliminary studies.” In addition to investigating complexing or sequestering agents, he also investigated several commercially available surfactants.

One example of early work on the use of organic additives is provided in a patent (Richard and Bowman, 1970) that describes the use of chelating agents (such as the tetrasodium salt of ethylenediaminetetracetic acid) to bind di- and trivalent ions in the process water and thereby improve the bitumen/water and bitumen/solids ratios in the primary froth.

Richard’s experimental work led him to a considerable number of ideas and conclusions about the hot water process, some of which we summarize below by way of the following quotations.

“pH adjustment by the addition of caustic or sodium salts of weak acids . . . gave higher oil recovery and lower water and solids in the froth production with most tar sands.”

“Good quality tar sands (pH 8–9) after storage . . . result in low pH values and exhibit poor processibility. When pH was adjusted to alkaline conditions with NaOH, good processibility is regained . . . .”

“The optimum pH of the separation water phase was found to be about 9 . . . and appeared to be affected by the ionic strength of the water phase.”

“Organic surfactant additions in separations have indicated that only anionics, chelates and nonionics are effective. The improvements, however, are small, which may reflect the large amount of polar surfactant components already present in the tar sands. Utilizing these naturally occurring surfactants by suitable pH control and chemical modification appears to be the best route to better operations.”

Richard also recognized a problem that is closely related to the benefit that is derived from the presence of surfactants in the process water: “Although the results of this study are only approximate, they do show that the interfacial tension at about 180°F, the temperature of the Hot Water Separation Process, is very low and hence a condition for emulsification of oil and water exists . . . substantiated by the high water content of the froth.”

Before going on to summaries of more recent research on chemical properties of oil sands, we point out that Richard recognized the very important variability in

processibility of different samples of oil sands. He specifically noted a general correlation (with exceptions) of good processibility with low fines content and poor processibility with high fines content. He also noted that aging of mined oil sands often led to lower pH, increased concentrations of polyvalent ions in process water, and poor processibility, which sometimes could be improved by adding NaOH to increase the pH.

### **Bowman, Baptista, and Leja**

Bowman (1967) reviewed many of the chemical properties of Athabasca oil sands, with particular emphasis on interfacial properties, including specific mention of surfactants among the water soluble components of bitumen. Several of Bowman's conclusions are summarized in the following quotations.

"At a high pH, the complete dissociation of carboxylates, and the hydroxylation of the solid surfaces leads to high surface charges. The system is well dispersed and the attractions between particles are minimal. Although this is the optimum condition for prevention of oil/ solid association, the initial attachment of gas bubbles to bitumen is also made more difficult."

"The water-soluble organic material concentrates at air/water interfaces where it reduces the surface tension to values as low as 30 dynes/cm. The major functional group appears to be a metal carboxylate."

"The 'pH controlling' minerals in the Athabasca tar sands affect interfacial properties . . . calcite, siderite, ferrous hydroxide, and pyrrhotite will increase the pH and provide a system where the particles are negatively charged and well dispersed. Oxidation of the latter three minerals destroys this pH elevating effect. Oxidation of the sulphur minerals to sulphates will further reduce the pH."

" . . . some (but not all) of the desired transformations require a high temperature and a high pH. One notable exception is the initial attachment of gas bubbles to bitumen particles."

Baptista and Bowman (1969) showed that surfactants that aid flotation of bitumen and therefore can increase recovery of bitumen also aid the flotation of fine minerals, which has the undesirable effect of decreasing the quality of the froth obtained in the hot water process.



Bowman (1967) and Leja and Bowman (1968) have provided a useful start on application of thermodynamics to chemical reactions of minerals and also interfacial effects that are important in connection with processing mined oil sands.

## **MORE RECENT INFORMATION ABOUT SURFACTANTS AND PROCESSIBILITY OF MINED OIL SANDS**

### **Sanford and Seyer**

Following the work of Bowman and Leja and Bowman cited above, there was a period of uncertainty at Syncrude (Sanford, 1992) about the relative importance of the advantages and disadvantages to be attributed to surfactants. At that time there were problems with oil sands sticking to conveyor belts and it was discovered (Sanford and Shaw, 1979ab and 1980ab) that these problems could be eased by appropriate use of surfactants. Because of reasonable concern that adding surfactants to remedy this problem of oil sand sticking to conveyor belts might diminish the recovery of bitumen, several tests were carried out. These tests provided confirmatory evidence that surfactants lead to an overall improvement in recovery of bitumen, and therefore provided part of the impetus for further investigations that are described later in this chapter and in following chapters.

Sanford and Seyer (1979) have described the "batch extraction unit" or "BEU" that has been used extensively at Syncrude for laboratory investigations of the hot water separation process. They also reported experimental results that illustrated the importance of added sodium hydroxide and related production of surfactants. Patents based on work of Sanford (1980 and 1981abc) were concerned with alkaline process aids (such as NaOH) that act partly by reaction with certain components of bitumen to produce "natural" surfactants. Sanford (1983) has summarized information in these patents (especially 1981a) along with results of other laboratory and pilot plant investigations of recovery of bitumen from samples of oil sand having different compositions and with different choices of process variables, such as amount of sodium hydroxide added. Sanford (1983) has also used many of these results as the basis for a model of the separation process that has led to a useful correlation of ore characteristics and process variables with bitumen recovery. We will discuss these experimental results and Sanford's model later in this chapter and also in Chapter 8.



## **Tailings and Surfactants**

Several investigations of surfactants derived from bitumen have been undertaken because of specific interest in the properties of tailings from the hot water processing of mined oil sands — see Kasperski (1992) for a general review of tailings, including investigations of surfactants in tailings water. Here we will cite only a few investigations that have provided background information that is useful in connection with our present interest in processibility.

Moschopedis et al. (1977 and 1980) used solvent extraction with methylethylketone to separate what they called asphaltic acids from acidified tailings water. Their elemental analyses of extracted material showed considerably more oxygen than the average oxygen content of whole bitumen. Spectroscopic investigations and measurements of surface tensions led them to conclude that many of the water soluble compounds contained carboxylic acid groups, and also suggested the presence of “oxygenated sulphur groups.” Results of more recent research lead to the conclusion that many or most of these latter groups are sulfonates.

Ali (1978) applied foam fractionation (previously mentioned by Bowman, 1967) to separate surface-active compounds from process water. Subsequent separations and analytical measurements have provided evidence that these surface-active substances include salts of carboxylic acids and sulfur-containing substances that have been described as sulfonic acids or sulfoxides.

Burchfield and Hepler (1979) used diethyl ether for solvent extraction of dissolved organics from tailings water. Results of subsequent measurements of surface tensions and spectroscopic investigations were consistent with earlier and later conclusions concerning the general properties of water-soluble surfactants derived from bitumen.

## **Interfacial Science**

Takamura (1985) and Takamura and Chow (1985) have investigated application of the “Ionizable Surface-Group Model” to the electric properties of the bitumen-water interface and related effects on the recovery of bitumen from mined

oil sands. Their theoretical work in combination with results of measurements of electrophoretic mobilities of droplets of bitumen suspended in aqueous solutions led them to conclude that the surface charges of bitumen under different conditions (variable pH and concentration of salt dissolved in water) can be explained in terms of dissociation of carboxylic acids. This general approach has been used as part of the basis for a theory to describe and permit understanding of the hot water process for separating bitumen from mined oil sands, as described by Takamura and Wallace (1988). Some aspects of this description have been criticized by Czarnecki and Smith (1990) and defended by Wallace et al. (1990). In Chapter 8 we return to discussion of these and related models and theories of the hot water process for separating bitumen from mined oil sands.

Dobrogowska and Hepler (unpublished) have measured interfacial tensions of two phase systems in which one phase consisted of 5% bitumen in toluene and the other phase was an aqueous solution of specified pH and salt content. In some cases the bitumen was subjected to oxidation by air. Results of all this work (see Chapter 4) led to the conclusion that there are surface-active constituents in bitumen and that some or most of these surface-active substances are carboxylic acids. It was also concluded that mild oxidation of bitumen leads to production of more (possibly different) surfactants. See Chapter 7 for a report on some recent research on production of surfactants by alkaline oxidation of bitumen and the possible use of these surfactants in processing mined oil sands.

## **Utah Tar Sands**

There are important differences between the Athabasca oil sands and those in Utah. Among the differences that are most important with respect to processing mined oil sands are the generally larger viscosities of Utah bitumen and the smaller water contents of Utah tar sands. Along with these differences, there are enough similarities to justify relating information about either oil/tar sand to information about the other. Accounts of various investigations of the Utah tar sands are cited elsewhere in this book; here, we cite only two reports that are specifically concerned with interfacial properties that are related to the effects of surfactants.

Misra et al. (1981) have used spectroscopic and potentiometric methods to identify paraffinic carboxylates (surfactants) in process water and suggested that these carboxylates account for the polarity of the surface of bitumen and thence the hydrophilic (water attracting) character of the bitumen that is being digested in the Utah version of the hot water process. Results of measurements of contact angles led to the suggestion that phase separation by flotation of bitumen is dependent on air bubble entrapment by bitumen droplets rather than attachment of bubble to bitumen. These workers also suggested that addition of too much sodium hydroxide as process aid should be avoided because of consequent production or release of too much surfactant by chemical reaction of acidic components of bitumen with hydroxide ions.

Further investigations that included measurements of electrophoretic mobilities by Hupka and Miller (1991) showed that surfaces of Utah bitumen, sand particles, and clay particles are all negatively charged under the alkaline conditions usually encountered in the hot water process. The negative charges on the surfaces of bitumen and sand lead to repulsions that aid the separation of the bitumen from the sand. On the other hand, it was observed that the negative charges on bitumen and on clay particles are not sufficient to lead to easy separation of these components of Utah tar sands. These investigators have also plotted their "coefficient of separation" against the concentration of NaOH and observed a maximum, which provides further evidence that recovery of bitumen is diminished by addition of too much sodium hydroxide.

The general ideas presented by Misra et al. (1981) and by Hupka and Miller (1991) concerning "too much" sodium hydroxide and surfactant are consistent with ideas developed by Smith and Schramm as a result of their investigations of hot water processing of mined Athabasca oil sands. Smith and Schramm have referred to a "critical concentration" of surfactant and have shown that either larger or smaller concentrations of surfactant usually lead to reduced recovery of bitumen. They have also shown that the concentration of surfactant in solution is related to the amount of added sodium hydroxide and to polyvalent minerals present in the oil sands. All of this work by Smith and Schramm is discussed in some detail later in this chapter and in subsequent chapters.

Hupka and Miller (1991) have related zeta potentials (obtained from electrophoretic mobilities — see Chapter 4) to rates of flotation of bitumen and of clay.

### **Sources of “Natural” Surfactants**

Many of the results cited in this section are consistent with the general idea that some components of bitumen are soluble in water, that most of the solubilities are dependent on pH, and that some of these water-soluble substances are surfactants. It has also been clear for some time that the surfactants that are naturally in bitumen and especially those that are produced by reaction of bitumen with aqueous bases are important in the hot water process for separating bitumen from mined oil sands.

It is likely that some or most of the surfactants or precursors of “natural” surfactants are naphthenic acids (or other carboxylic acids) in the bitumen. These unionized naphthenic acids are only very slightly soluble in acidic solutions and have low surface activity, but the carboxylate anions (negatively charged) formed by reaction of these carboxylic acids with sodium hydroxide are more soluble and are effective surfactants.

It is also possible that some of the “natural” surfactants that are important in the hot water process are originally present as polyvalent metal (magnesium, calcium, iron) salts of naphthenic or other carboxylic acids, with these carboxylate salts being associated with some of the minerals in the oil sand. As shown later in this book, sodium hydroxide can react with some mineral components of oil sands in ways that can liberate such carboxylate salts.

### **Directions of Further Research on Surfactants, Minerals, and the Role of Sodium Hydroxide in Processing Mined Oil Sands**

Along with the important generalities about surfactants mentioned above, we have long had useful but incomplete specific knowledge about some of the practical consequences of such factors as addition of sodium hydroxide and the resulting high pH of process water. Further research, to be described in following sections of this chapter and in subsequent chapters, has been intended to provide useful information about the following subjects:



- (i) Much emphasis has been placed on ascertaining the optimum amount of sodium hydroxide to add to various "grades" of oil sand to obtain the maximum recovery of bitumen. In this connection, "grades" has been expected to include consideration of the bitumen content, fines content, and possibly the presence of other minerals.
- (ii) Research (especially at Syncrude) has been intended to provide specific information about the optimum concentration of natural surfactants that will lead to maximum recovery of bitumen and about the amount of added sodium hydroxide that will lead to this optimum or "critical" concentration.
- (iii) Other research to be discussed in this chapter and in subsequent chapters has been intended to lead to information about the consequences of chemical reactions of minerals with sodium hydroxide.
- (iv) Early research (especially by Bichard and Bowman, as already cited) showed that aged (after mining) oil sands usually have lower pH than do freshly mined oil sands and that these aged oil sands are usually more difficult to process than are similar fresh oil sands. These early investigators also showed that some of the consequences of aging could be reversed by using more than the usual amounts of sodium hydroxide as process aid. Some more recent research has been directed at understanding the earlier observations and thence to designing appropriate storage and processing procedures.

## **SOME RECENT RESEARCH ON SURFACTANTS AND PROCESSIBILITY AT SYNCRUDE**

Now we turn to detailed discussion of recent research at Syncrude (mostly by Schramm and Smith) that has been reported during the period 1984-1989. This research was directed toward separation of naturally occurring surfactants, partial chemical characterization of these surfactants, and analyses of surfactants in relation to optimum recovery of bitumen from mined oil sands.

An early reference to a "critical" concentration of natural surfactant contained in bitumen or derived by reaction of bitumen with sodium hydroxide is provided in a patent by Schramm and Smith (1984) who wrote "The present invention is based on



the discovery that there is a critical level of free surfactant in solution in the aqueous phase of the drum slurry which always is required to obtain maximum recovery of bitumen . . . in the primary froth.”

The important operating principles based on this work by Schramm and Smith (1984) can be summarized by the following quotation. “The process in accordance with the invention therefore comprises: (a) determining, for a single tar sand type and the extraction circuit used, the free surfactant content in the aqueous phase of the slurry, which will yield the maximum primary . . . recovery; (b) monitoring the free surfactant content in the aqueous phase of the slurry during subsequent processing of various types of tar sand feed in said circuit; and (c) varying the process aid addition to the slurry as the nature of the tar sand feed varies, to maintain said free surfactant content substantially at the level which leads to maximum primary bitumen froth recovery.” The process aid mentioned in (c) is sodium hydroxide.

This patent (Schramm and Smith, 1984) also includes description of their method for separating and analyzing for surfactants in process water; we return to this subject later in this section.

A patent based on work by Smith and Schramm (1984) is also concerned with the relationship between operating variables and surfactants derived from bitumen, as illustrated by the following quotation. “Two or more tar sand feeds are blended in specified proportions in combination with a specified dosage of NaOH to provide a slurry, having a free surfactant content dissolved in the aqueous phase of the slurry, which yields the maximum possible primary froth production from the hot water extraction process.” This patent also contains description of experimental methods for separating and analyzing surfactants.

Schramm and Smith (1984) and Schramm, Smith, and Stone (1984ab) have provided detailed descriptions of the experimental procedure developed at Syncrude for the detection and analysis of anionic (negatively charged) surfactants in the aqueous phase of the hot water process; Appendix 3 in this book contains specific directions for laboratory operations, along with example calculations. Several other publications from Syncrude (Schramm, Smith, and Stone, 1985; Schramm and Smith, 1985, 1987abc, and 1989) provide further information about their methods for

investigating surfactants in bitumen-water systems and results of such investigations. We also mention that Schramm, Smith, and Stone (1984a) have reviewed earlier methods for analyzing surfactants in aqueous systems.

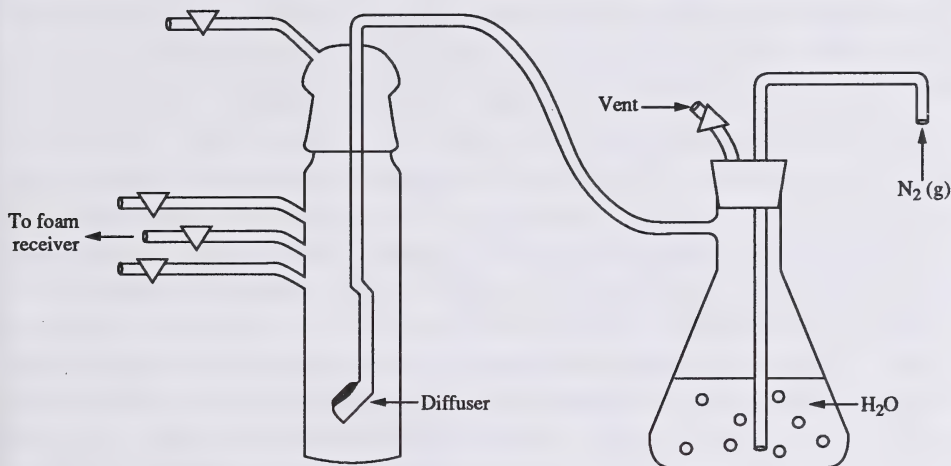
The Syncrude method for detecting, analyzing, and partially characterizing surfactants in bitumen-water systems is described in the following paragraphs. In this connection it should be recognized that part of the need for the procedure developed at Syncrude comes from the presence of bicarbonate ions as well as carboxylate surfactants in the process water.

Part of the analytical procedure involves titration of a sample of process water with aqueous hydrochloric acid. An end point is observed at pH close to 4.5, corresponding to the sum of the carboxylate and bicarbonate concentrations. Further acidification to still lower pH and sparging with nitrogen removes all of the bicarbonate as gaseous carbon dioxide. After the resulting solution is made alkaline by addition of sodium hydroxide, another titration with aqueous hydrochloric acid yields another end point at pH close to 4.5, which can be attributed to carboxylates (without bicarbonate). Combination of results of these two titrations can establish the concentrations of both bicarbonate and carboxylate in the process water. It should be noted that this procedure leads to the total concentration of carboxylates in the process water; some of these carboxylates may not be surface-active.

The procedure described above does not distinguish between surface-active and surface-inactive carboxylates, nor does it yield information about surfactants such as sulfonates that are present as surface-active anions in both alkaline and acidic solutions. Because of these limitations, the next steps in the separation and analysis procedure were developed as follows.

Foam fractionation with apparatus illustrated in Figure 3.1 has been used to separate surfactants from samples of process water. This fractionation procedure is usually continued until the surface tension of the process water approaches the surface tension of pure water, thus indicating that most surface-active solutes have been removed.

The collapsed foam obtained in this way was then analyzed as follows.



**Figure 3.1.** Sketch of the foam fractionation column and nitrogen humidifier used to concentrate surface active compounds from supernatant secondary tailings.

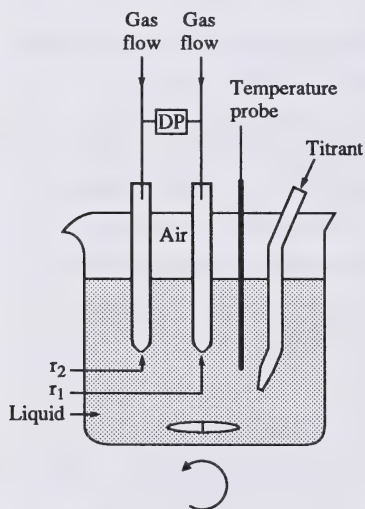
First, an aliquot sample of collapsed foam in water was titrated with aqueous hydrochloric acid. Because the collapsed foam contains little or no dissolved bicarbonate, the end point at pH close to 4.5 corresponds entirely or mostly to the concentration of surface-active carboxylates extracted from the process water. The difference between the *total* concentration of carboxylates obtained as a result of the earlier titrations of a sample of process water and the concentration of surface-active carboxylates obtained as a result of this subsequent titration of collapsed foam leads to the concentration of surface-inactive carboxylates.

Although the method described above is sound in principle and works well for some solutions of surfactants, it has been found to be inadequate for accurate measurement of the small concentrations of surfactant that are especially important in the hot water process. Further, this method provides no information about sulfonates or other surfactants that are present as anions in both acidic and alkaline solutions and thence show no end-point in an acid-base titration. These inadequacies in the method described here led to further developmental work as follows.

Another analytical procedure involves titration of a solution containing anionic (negatively charged) surfactants with a stock solution of a cationic (positively

charged) surfactant, with progress of the titration being monitored by measurement of the surface tension of the solution being titrated. Researchers at Syncrude have used cetyltrimethylammonium bromide (often called CETAB) as the cationic surfactant and have monitored the surface tension by using the maximum bubble pressure method (apparatus illustrated in Figure 3.2). This kind of titration with the solution having  $\text{pH} > 4.5$  yields the total concentration of surfactants. Repeating this titration on another aliquot at lower  $\text{pH}$  (about 3) yields the concentration of sulfonates (or other strong acid surfactants) because at this low  $\text{pH}$  the carboxylates are converted to the un-ionized carboxylic acids, which are much less surface-active than the anionic sulfonates and carboxylates.

The analytical methods described above have been applied to tailings water, to process water from the industrial plant, and especially to process water from the Syncrude batch extraction unit that is the principal tool used to investigate effects of several operating variables on processability. Now we provide a chronological (beginning in 1984) summary of some conclusions about the effects of surfactants on recovery of bitumen by hot water flotation.



**Figure 3.2.** Schematic diagram of the cell used for the titration of anionic surfactants with a cationic surfactant. The surface tensiometer probes are shown to the left.

The most-used experimental approach at Syncrude has involved processing several samples of a particular batch of homogenized oil sands under different conditions, with the amount of added sodium hydroxide being the variable of greatest interest here. The intent has been to obtain information about the amount of sodium hydroxide that will lead to maximum recovery of bitumen from oil sands having different characteristics such as percent bitumen, fines content, etc. Much of the focus has been on sorting out the complex relationships between characteristics of oil sand, amount of sodium hydroxide added, concentration of surfactant in process water, and recovery of bitumen.



Schramm, Smith, and Stone (1984a) used their analytical methods to find that the amounts of "free" surfactants in process water are linearly related to the amounts of sodium hydroxide added to a particular "grade" of oil sand and that the amounts of carboxylate surfactants are usually about twice the amounts of sulfate or sulfonate surfactants. At about this same time, Schramm and Smith (1984a) and Schramm, Smith, and Stone (1984b) provided more information about concentrations of surfactants in process water and also showed that recovery of bitumen is directly related to the concentration of surfactants in the process water. More specifically, they found that maximum recovery typically occurred when the concentration of surfactants derived from reaction of bitumen with sodium hydroxide was about  $1 \times 10^{-4} \text{ mol L}^{-1}$ . Further evidence to support their idea that there is a "critical concentration" of surfactants for maximum recovery has followed from subsequent research at Syncrude (cited below) and also from research on Utah tar sands by Misra et al. (1981) and Hupka and Miller (1991).

Because the amounts of surfactants formed are related to the amounts of sodium hydroxide added as process aid, it follows that maximum recovery of bitumen is usually associated with addition of some "critical" amount of sodium hydroxide; using either too much or too little sodium hydroxide as process aid often causes the percentage recovery of bitumen to fall below the optimum value.

Here we emphasize that the amounts of sodium hydroxide required to lead to the critical concentration of *free* surfactant are different from one grade of oil sand to another for reasons that are discussed later in this chapter and also in Chapters 5 and 6.

Schramm and Smith (1985) have investigated electrophoretic mobilities (see Chapter 4 for a description of this method) of droplets of bitumen in process water and have observed that the negative charge on these droplets can be correlated with the previously mentioned critical concentration of free surfactant in solution. It is also emphasized in their paper that the concentration of free surfactant is more directly important than other variables (such as pH or amount of sodium hydroxide added) for determining percentage recovery of bitumen. All of these results are consistent with the general idea that negative charge on the bitumen benefits separation of bitumen from the minerals that also have negative surface charges under the usual operating conditions for the hot water flotation process.



Schramm and Smith (1985) have extended their earlier investigations of the relationships between amount of added sodium hydroxide, concentration of produced surfactants, and processibility to include other variables such as temperature and input of mechanical energy. They showed that reducing the temperature of slurring (conditioning) from 82°C to 55°C led to only small changes in the previously observed correlation between bitumen recovery and concentration of *free* surfactant. Results of experiments with various slurring times (and related inputs of mechanical energy) showed that it requires longer times and therefore more mechanical energy input to obtain maximum recovery at 55°C than at 82°C. An important general conclusion of this work is that overall maximum recovery of bitumen is related to several operating variables, including temperature, slurry concentration, slurring time, and free surfactant concentration, with this last quantity being determined partly by the amount of sodium hydroxide added as process aid.

During later investigations of processibility of various Athabasca oil sands, Schramm and Smith (1987ab) observed that graphs of primary recovery of bitumen against amount of sodium hydroxide added (other conditions constant) to some samples of Athabasca oil sands showed two maxima at approximately 0.02 and 0.055 weight percent added sodium hydroxide. Further investigations of concentrations of free surfactants in process water and electrophoretic mobilities yielded information that led to the following conclusions. (i) As found previously, there are two classes (carboxylates and sulfates-sulfonates) of natural surfactants; (ii) Surfactants of each class are capable of promoting efficient flotation of bitumen, if the concentration of free surfactant is at or near its critical concentration; (iii) The sulfate-sulfonate surfactants are effective only when the concentration of carboxylate surfactants is very small.

Schramm, Smith, and Stone (1985) have investigated the processibility of mixtures of Athabasca oil sands of different grades. First, they observed that bitumen recovery from such mixtures was a non-linear function of recoveries obtainable by processing the different grades of oil sand separately. A potentially important conclusion is that more bitumen can be recovered from a mixture of high grade oil sand with low grade oil sand than from the same amounts of the two grades processed separately, provided that less than about 60% of the mixture is made up of the low grade oil sand. Combination of results of recovery determinations with

analysis for natural surfactants (carboxylates) derived from reaction of bitumen with added sodium hydroxide led to the important conclusion that fine clay minerals are detrimental to the flotation process because they adsorb surfactants and therefore tend to make the free surfactant concentration less than the critical value for maximum recovery. This explanation accounts for the earlier observation of several researchers that it is often possible to increase recovery of bitumen from low grade oil sands (containing relatively large amounts of fine clay minerals) by using more than the usual amount of sodium hydroxide as process aid; this "extra" sodium hydroxide leads to formation of more carboxylates, thus compensating for effective loss of some surfactant by adsorption on fines. It should also be recognized that "extra" sodium hydroxide can be required because some of the added sodium hydroxide can react with various minerals (as discussed in the following section), which can decrease the amount of hydroxide available to react with bitumen to produce surfactant.

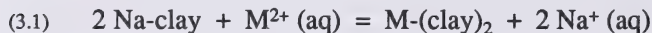
### **THE INFLUENCE OF DI- AND TRIVALENT POSITIVELY CHARGED IONS AND THEIR COMPOUNDS ON PROCESSIBILITY**

It is well known that the mineral constituents of oil sands have an important bearing on the recovery of bitumen by the hot water process and also on some alternatives to the hot water process. Investigations cited earlier in this chapter have provided evidence that some of the effects of fine clay minerals on recovery of bitumen are due to adsorption of surfactants, which means that these surfactants are not available to aid in the separation of bitumen from silica and possibly other minerals. It has also been shown that this problem can be remedied, at least partly, by adding more sodium hydroxide, which leads to production of more surfactants.

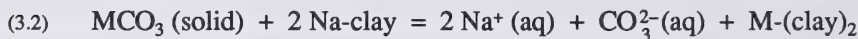
Other investigations, which we consider now, have been concerned with effects of chemical reactions (as contrasted with adsorption) involving di- and trivalent positively charged ions and their solid compounds on processibility.

Overall chemical analyses of many samples of oil sands have shown that most such samples contain small (relative to silica) amounts of such di- and trivalent elements as calcium, magnesium, and iron, but such overall elemental analyses do not tell us how these elements occur. We do know, however, that carbonate minerals

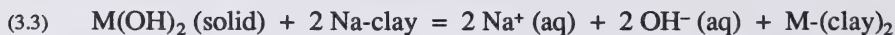
of calcium, magnesium, and iron have been identified in many samples of oil sands and that iron sulfide minerals have been identified in some samples. There is also the possibility that positively charged di- and trivalent ions are associated with clays as a result of ion exchange reactions. For example, a "natural" clay in the common sodium form can undergo cation exchange with a divalent ion in solution as represented by the chemical equation



It is known (Ewin et al., 1981) that equilibrium constants for reactions of type (3.1) are moderately large, which means that presence of any reasonable concentration of  $\text{M}^{2+}(\text{aq})$  in connate water or in process water can lead to formation of the divalent clay represented here by  $\text{M-clay}_2$ . There is also the possibility of ion exchange between sodium clay and solid hydroxides and carbonates as represented by



and



The extents of these reactions are dependent on pH and on whether M represents  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ , or  $\text{Fe}^{3+}$ .

Some of Bichard's pioneering research (1987) was concerned with the properties of minerals and polyvalent metal ions in relation to recovery of bitumen. He showed that adding sequestering or complexing agents that bind such ions as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Fe}^{3+}$  leads to improved recovery of bitumen from some oil sands. In this connection, also see the patent by Bichard and Bowman (1970).

An early review by Bowman (1967) has provided a thermodynamic explanation for how positively charged di- and trivalent ions derived from minerals in the oil sands can appear in the process water. More recently, Baptista (1989ab) has summarized his research on effects associated with presence of polyvalent ions, as

discussed further in following paragraphs. We also have evidence (Kasperski, 1992) that polyvalent ions (especially iron) have a significant effect on the properties of tailings that result from the hot water process.

Baptista (1989ab) developed a method for separating clays from the tailings and middlings, and then measured the cation exchange capacities of these separated minerals. As a result of these separations and measurements, Baptista was able to show that recoveries of bitumen from the Syncrude batch extraction unit (BEU), the Syncrude pilot plant, and the Syncrude commercial plant were all inversely correlated with the ion exchange capacities (Ca and Mg) of the clays. This conclusion is an important supplement to the previously observed correlation of recovery of bitumen with the inverse of the clay content for many (but not all!) oil sands.

Baptista specifically noted (1989b) that among his samples of oil sand the sample that gave the best recovery of bitumen was the sample with the largest fines content (contrary to the earlier generalization mentioned above), which also had the smallest cation exchange capacity for calcium. He also noted that the sample of oil sands that gave the poorest recovery of bitumen had the largest cation exchange capacity for calcium, but had only average overall fines content.

Baptista (1989b) was also concerned with amorphous iron oxide/hydroxide coatings on fine minerals because of previous knowledge that these amorphous substances in the wet state can form highly hydrated gels that can link or "loosely cement" clay particles together in three-dimensional structures that can trap both oil and water. Although there is some evidence that this ability of amorphous iron oxides/hydroxides to form gels with clays is important with respect to oil sands tailings, Baptista was especially concerned with the possible connection between iron oxides/hydroxides and processibility. Results reported by Baptista (1989b) show that there is an inverse correlation between recovery of bitumen and amorphous iron oxide/hydroxide content. He also presented evidence that it is the accumulation of this amorphous material in the middlings that promotes gel formation and thence interferes with separation of the bitumen.

We also mention that Baptista reported (1989b) that an aged oil sand had a larger cation exchange capacity than did the same oil sand when fresh. This observation is consistent with his inverse correlation of recovery of bitumen with



cation exchange capacity and the common observation that recovery of bitumen from aged oil sands is often lower than recovery from a similar fresh sample.

Baptista (1989b) also showed that removing the amorphous iron oxide/hydroxide material that he considered to be coating the clays led to an increase in the fraction of solids smaller than 2  $\mu\text{m}$ , which was interpreted as supporting the idea that the amorphous material "cemented" fine particles together.

Very recent thermodynamic calculations by Tardy and Duplay (1992) have provided independent support for Baptista's evidence that clays containing divalent exchangeable cations form water-rich gel-like structures that interfere with the hot water process for flotation and thence separation of bitumen from sand.

In an earlier study of the effects of aging on processibility, Sanford (1983) observed that recovery of bitumen decreased with aging and that aging was also correlated with an increase in fines ( $<44 \mu\text{m}$ ) content. This correlation is consistent with the production of acid by oxidation of sulfide minerals (especially pyrite) and reaction of acid with amorphous iron oxides/hydroxides that have been investigated by Baptista (1989b).

Smith and Schramm (1989) have investigated the processibility of mined oil sands that are contaminated with overburden material and have established that the generally poor processibility of such contaminated feed stock is due to the presence of polyvalent metal ions derived from the overburden material. They have presented evidence to support their suggestion that these metal ions can affect processibility in two ways: (i) reacting with sodium hydroxide, thus preventing the sodium hydroxide from reacting with bitumen to produce carboxylate surfactants; (ii) precipitated metal hydroxides or free metal ions can adsorb or react with carboxylate surfactants, thus making these surfactants unavailable for assisting the separation of bitumen from minerals and the subsequent flotation of bitumen.

Further research on the combination of problems involving consumption of sodium hydroxide and production and adsorption of surfactant has been carried out by Smith at Syncrude, with results and conclusions that are reported in Chapters 5 and 6. Here we offer only the summarizing statement that results of this recent research are also consistent with the general conclusion that metal ions affect processibility because they consume sodium hydroxide (because of precipitation of

metal hydroxides) and can also tie up surfactants as a result of adsorption and possibly also direct chemical reactions leading to precipitation of surfactant, just as soaps (carboxylates) are often precipitated from hard water.

### **Aging of Mined Oil Sands**

The important early work of Clark and Pasternack (1949) that was concerned with several aspects of the role of fine minerals in the hot water process included investigations of the effects of storage time of mined oil sands on processibility. Their results showed that aged (after mining) oil sands differ from freshly mined oil sands in two important respects: (i) hot water processing of aged oil sands leads to produced froth containing more suspended fine mineral matter than does similar processing of freshly mined oil sands; (ii) recovery of bitumen is often lower for aged oil sands than for freshly mined oil sands.

Bichard (1987, based on research during the period 1957–1965) and Bowman (1967) noted that aging leads to a decrease in pH and proposed that this decrease is largely due to oxidation of sulfide minerals, leading to production of dilute sulfuric acid. Reaction of this acid with carbonate minerals leads to presence of more positively charged polyvalent metal ions in process water. More recently, Sanford (1983) has confirmed the correlation between aging, positively charged di- and trivalent ions in solution, and decreased recovery of bitumen.

Sanford's (1983) work on processibility was partly concerned with aging, and was discussed earlier in connection with the correlation he observed between decline in processibility and increased fines content.

Schramm and Smith (1987bc) have carried out extensive investigations of the effects of aging on processibility of mined oil sands. Their results led them to conclude that air-induced oxidation of minerals (especially pyrite,  $\text{FeS}_2$ ) led to decreased pH and increased concentrations of polyvalent metal ions. The presence of acid leads to a requirement for increased NaOH to reach the optimum alkaline pH. The presence of polyvalent metal ions also leads to a requirement for more NaOH, since these polyvalent ions react with hydroxide ions to precipitate polyvalent hydroxides. It is also possible that these polyvalent ions react with and precipitate

anionic surfactants, which leads to a still further requirement for additional NaOH to produce more natural surfactant by reaction with certain components of bitumen. Schramm and Smith (1989c) cited the earlier work of Wallace and Henry (see the following paragraph) and specifically noted that measuring the concentration of sulfate gives a measure of the extent of aging and related effect on processibility.

Because oxidation of sulfide minerals leads to lower pH (as noted by Bichard, Bowman, Schramm, Smith, and others), Wallace and Henry in 1984 (cited by Wallace, Henry, and Takamura, 1989) anticipated that the concentration of sulfate in oil sand might provide a useful indication of the extent of oxidation and thence the extent of aging. Subsequent determinations of bitumen recovery and sulfate content confirmed that sulfate concentrations do provide a useful indication of extent of aging, probably because the sulfate concentration is related to production of acid due to oxidation and also to related increased content of polyvalent ions in solution.

The investigations of Wallace et al. (1989) led them to write "It can be concluded therefore that as much deterioration in the oil sand will occur in two months storage at +20°C as in seven years at -18°C." These researchers and also Schramm and Smith (1987bc) found that oxygen naturally present in oil sands or introduced during mining is sufficient to initiate oxidation (rate increases dramatically with increasing temperature) and also found that oxidation can continue in the absence of oxygen so long as  $\text{Fe}^{3+}$  is present.

## REFERENCES

- Ali, L.H. Surface-active agents in the aqueous phase of the hot-water flotation process for oil sands, *Fuel* (1978) 57, 357-360.
- Baptista, M.V. Role of the exchangeable cations of oil sand clays in oil sand processing — part 1. Batch tests, *AOSTRA J. Research* (1989a) 5, 237-241.
- Baptista, M.V. Role of the exchangeable cations and iron-amorphous coatings of the oil sand solids in oil sand processing — part 2. Pilot and plant tests, *AOSTRA J. Research* (1989b) 5, 243-256.

- Baptista, M.V., and Bowman, C.W. The flotation mechanism of solids from the Athabasca oil sands, (1969) Preprint, 19th Canadian Chemical Engineering Conference, Edmonton.
- Bichard, J.A. *Oil sands composition and behavior research: the research papers of John A. Bichard, 1957-1965*, (1987) Alberta Oil Sands Technology and Research Authority, Edmonton.
- Bichard, J.A., and Bowman, C.W. Chelating agents in bituminous sand water process. (1970) U.S. Patent 3,522,168.
- Bowman, C.W. Molecular and interfacial properties of Athabasca tar sands, Proceedings, 7th World Petroleum Congress (1967) 3, 583-603.
- Burchfield, T.E., and Hepler, L.G. Some chemical and physical properties of tailings water from oil sands extraction plants, Fuel (1979) 58, 745-747.
- Clark, K.A., and Pasternack, D.S. The role of very fine mineral matter in the hot water separation process as applied to Athabasca bituminous sand, Research Council of Alberta, (1949) Report No. 53.
- Czarnecki, J., and Smith, R. Comments on "The physical chemistry of the hot water process", by K. Takamura and D. Wallace, J. Can. Petrol. Technol. (1990, November Supplement) 29, 72-73.
- Dobrogowska, C., and Hepler, L.G. Unpublished research.
- Ewin, G.J., Erno, B.P., and Hepler, L.G. Clay chemistry: investigation of thermodynamics of ion exchange reactions by titration calorimetry. Can. J. Chem. (1981) 59, 2927-2933.
- Hupka, J., and Miller, J.D. Electrophoretic characterization and processing of Asphalt Ridge and Sunnyside tar sands, Int. J. Mineral Processing (1991) 31, 217-231.
- Kasperski, K.L. A review of properties and treatment of oil sands tailings, AOSTRA J. Research (1992) 8, 11-53.
- Leja, J., and Bowman, C.W. Application of thermodynamics to the Athabasca tar sands, Can. J. Chem. Eng. (1968) 46, 479-481.



- Misra, M, Aguilar, R., and Miller, J.D. Surface chemistry features in the hot water processing of Utah tar sand, *Separation Sci. and Technol.* (1981) 16, 1523–1544.
- Moschopedis, S.E., Fryer, J.F., and Speight, J.G. Water-soluble constituents in Athabasca bitumen, *Fuel* (1977) 56, 109–110.
- Moschopedis, S.E., Schulz, K.F., Speight, J.G., and Morrison, D.N. Surface-active materials from Athabasca oil sands, *Fuel Proc. Technol.* (1980) 3, 55–61.
- Pasternack, D.S., and Clark, K.A. The components of bitumen in Athabasca bituminous sand and their significance in the hot water separation process, *Research Council of Alberta*, (1951) Report No. 58.
- Sanford, E. Process aid addition in hot water process based on feed fines content, (1980) U.S. Patent 4,201,656.
- Sanford, E. Method for addition of alkaline process aids to the conditioning step of the hot water process for extraction of hydrocarbons from bituminous sands, (1981a) Canadian Patent 1,094,003.
- Sanford, E. Aids for the conditioning step in the hot water extraction process for tar sands, (1981b) Canadian Patent 1,094,483.
- Sanford, E. Process aids for the conditioning step in the hot water extraction process for tar sand, (1981c) Canadian Patent 1,100,074.
- Sanford, E.C. Processibility of Athabasca oil sand: Interrelationship between oil sand fine solids, process aids, mechanical energy and oil sand age after mining, *Can. J. Chem. Eng.* (1983) 61, 554–567.
- Sanford, E.C. (1992) Personal communication.
- Sanford, E.C., and Seyer, F.A. Processibility of Athabasca tar sand using a batch extraction unit: the role of NaOH, *CIM Bull.* (1979, March) 72, 164–169.
- Sanford, E., and Shaw, R. Process of treating bituminous sands conveyor belt with release agents, (1979a) U. S. Patent 4,172,811.
- Sanford, E., and Shaw, R. Bitumen-sodium hydroxide-water emulsion release agent for bituminous sands conveyor belt, (1979b) U.S. Patent 4,146,125.

- Sanford, E., and Shaw, R. Non-ionic emulsifying release agent for bituminous sands conveyor belt, (1980a) U. S. Patent 4,197,939.
- Sanford, E., and Shaw, R.C. Release agent for bituminous sands conveyor belt, (1980b) Canadian Patent 1,085,554.
- Schramm, L.L., and Smith, R.G. Control of process aid used in hot water process for extraction of bitumen from tar sand, (1984) U.S. Patent 4,462,892.
- Schramm, L.L., and Smith, R.G. The influence of natural surfactants on interfacial charges in the hot-water process for recovering bitumen from the Athabasca oil sands, *Colloids and Surfaces* (1985) 14, 67–85.
- Schramm, L.L., and Smith, R.G. Two classes of anionic surfactants and their significance in hot water processing of oil sands, *Can. J. Chem. Eng.* (1987a) 65, 799–811.
- Schramm, L.L., and Smith, R.G. Some observations on the aging phenomenon in the hot water processing of Athabasca oil sands. Part 1. The nature of the phenomenon, *AOSTRA J. Research* (1987b) 3, 195–214.
- Schramm, L.L., and Smith, R.G. Some observations on the aging phenomenon in the hot water processing of Athabasca oil sands. Part 2. The mechanism of aging, *AOSTRA J. Research* (1987c) 3, 215–224.
- Schramm, L.L., and Smith, R.G. Some parametric studies of oil sand conditioning in the hot water flotation process, *AOSTRA J. Research* (1989) 5, 87–107.
- Schramm, L.L., Smith, R.G., and Stone, J.A. A surface tension method for the determination of anionic surfactants in hot water processing of Athabasca oil sands, *Colloids and Surfaces* (1984a) 11, 247–263.
- Schramm, L. L., Smith, R.G., and Stone, J.A. The influence of natural surfactant concentration on the hot water process for recovering bitumen from the Athabasca oil sands, *AOSTRA J. Research* (1984b) 1, 5–13.
- Schramm, L.L., Smith, R.G., and Stone, J.A. On the processibility of mixtures of oil sands, *AOSTRA J. Research* (1985) 1, 147–161.

- Smith, R.G., and Schramm, L.L. Blending tar sands to provide feedstocks for hot water process, (1984) U.S. Patent 4,474,616.
- Smith, R.G., and Schramm, L.L. Processibility of Athabasca oil sands by the hot-water process when contaminated with overburden material, *Fuel Proc. Technol.* (1989) 23, 215–231.
- Takamura, K. Physico-chemical characterization of Athabasca oil sand and its significance to bitumen recovery, *AOSTRA J. Research* (1985) 2, 1–10.
- Takamura, K., and Chow, R.S. The electric properties of the bitumen/water interface. Part II. Application of the ionizable surface-group model, *Colloids and Surfaces* (1985) 15, 35–48.
- Takamura, K., and Wallace, D. The physical chemistry of the hot water process, *J. Can. Petrol. Technol.* (1988, November–December) 27, 98–106.
- Tardy, Y., and Duplay, J. A method of estimating Gibbs free energies of formation of hydrated and dehydrated clay minerals. *Geochim. Cosmochim. Acta* (1992) 56, 3007–3029.
- Wallace, D., Henry, D., and Takamura, K. A physical chemical explanation for deterioration in the hot water processibility of Athabasca oil sand due to aging, *Fuel Sci. & Technol. Int.* (1989) 7, 699–725.
- Wallace, D., Chow, R., and Takamura, K. In support of “The physical chemistry of the hot water process”, *J. Can. Petrol. Technol.* (1990, November Supplement), 29, 74–75.

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***Physical Properties of the  
Components of Oil Sand and  
their Effects on Extraction***

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## **INTRODUCTION**

In this chapter we will examine briefly the hot water extraction of bitumen from oil sands and outline the detailed physical processes (or those thought to be involved) from both the bulk and microscopic perspectives. Recent research results from the Alberta Research Council and Syncrude Research Centre will be described, and discussed in terms of the influence that these properties have on the physical chemistry of oil sand conditioning, bitumen flotation, and froth treatment.

The *AOSTRA Technical Handbook on Oil Sands, Bitumens and Heavy Oils* (Hepler and Hsi, 1989) summarizes many of the properties and also the experimental methods that have been used in various investigations of oil sands. Measurements of the important physical properties for oil sands and oil sands process streams are not always straightforward. For example, in sampling the oil sand, difficulties may be experienced in obtaining a representative sample especially when the desired sample may be smaller than some of the rocks and clay lumps, so that the sampler may take material that does not contain a representative amount of rock and clay. Additional difficulties arise when sampling the process dispersions, which are also non-homogeneous and have some properties that change with time after sampling.

## **THE PHYSICAL CHEMISTRY OF THE COMMERCIAL BITUMEN RECOVERY PROCESS**

Operating and development targets for the commercial plants are the efficient separation of bitumen from the mineral matrix and efficient removal of the residual water and solids from the bitumen. In the commercial process, preparation of bitumen suitable for upgrading is carried out in the following three stages: oil sand conditioning, primary separation, and froth treatment.

**Oil sand conditioning:** Oil sand, hot water, low quality steam, and recycle water from the tailings pond are mixed gently in a tumbler into a slurry, at a temperature of approximately 80°C. A process aid (NaOH) is added to benefit the separation. It is thought that the added water mixes into the water which is already present as a film between the solids and the bitumen and expands the solids/bitumen matrix, so that the bitumen and solids can move apart in the subsequent flotation process. During conditioning, air is entrained as bubbles which become coated with

bitumen films; this enhances the bitumen flotation rate and is an important factor in the overall process (Schramm, 1989). On a microscopic scale, the conditioning is a balance of hydrodynamic forces imparted by the tumbler, the interfacial properties, and the slurry rheology.

**Primary separation:** The conditioned slurry is screened to remove oversized material (rocks, clay lumps, etc.) and mixed with additional water. It is then pumped to large primary separation vessels, where gravity separation is allowed to occur, with the aerated bitumen tending to rise, and the larger solids tending to sink. A complex three phase system (primary froth) consisting of water and solids dispersed in bitumen overflows from the top of the vessel. Sand and silt are removed from the bottom of the vessel as a dense aqueous slurry (tailings). The remainder, most of which is fine solids and some bitumen, is removed as an aqueous side-stream (middlings). Both the tailings and middlings are subjected to aeration for additional bitumen recovery. The bituminous froth (secondary froth) recovered by forced aeration is usually of higher solids and water content than the primary froth. Because primary froth tends to have higher quality (i.e., lower solids and water content) than secondary froth, there is an incentive to maximize the fraction of the total bitumen recovered in the primary separation.

Under the nearly quiescent conditions within the primary separation vessel, the velocity of the rising aerated bitumen and settling solids can be described by the Stokes' equation (Schramm, 1989). For spherical droplets of radius "a" this can be expressed as

$$(4.1) \quad v = \frac{2}{9} \frac{(\rho(s) - \rho) g a^2}{\eta}$$

where  $\rho(s)$  and  $\rho$  are the densities of the suspended and continuous phases, respectively,  $g$  is the acceleration due to gravity, and  $\eta$  is the viscosity of the continuous phase. Extensions of Stokes' equation that are valid for higher Reynolds number such as Swanson's equation (Swanson, 1967,1975) may be more applicable for this situation (Danielson, 1990). Nevertheless, the Stokes equation can be used as a basis for discussion of the properties that are important in gravity separation.

The velocity is expected to be proportional to the density difference between the particle (aerated bitumen) and the medium (clay-in-water dispersion), proportional to the square of the particle radius, and inversely proportional to the viscosity of the medium. The aerated bitumen particles take the form of air bubbles surrounded by a thin film of bitumen (Bowman, 1969). The size and average density of a particular bitumen coated air bubble are determined by the size of the air bubble. The size of the air bubble is determined during conditioning and is controlled mainly by the mechanical agitation in the tumbler, and the surface and interfacial tensions. The viscosity of the middlings is dependent upon the concentration of solids and their state of dispersion.

Non-floating bitumen in the middlings, primary tailings, and secondary tailings may be (a) "free" bitumen which has not been aerated because there was an insufficient number of bubbles to pick up all the bitumen droplets, (b) aerated bitumen which had insufficient residence time to reach the froth, (c) bitumen which was aerated but became detached from its bubble, (d) "free" bitumen with surface properties which prevented air attachment, or (e) bitumen which remained attached to the solids. The distribution of the bitumen amongst these states is determined by mechanical conditions, interfacial properties, and the viscosity of the continuous phase.

There is a phase inversion somewhere in the separation sequence. As the aerated bitumen droplets rise in the primary separation vessel, a concentrated oil-in-water cream forms. Water and solids drain from this cream until some critical conditions are reached, at which point bitumen becomes the continuous phase, and further drainage of water and solids ceases. The critical conditions are probably related to the stability of the film of water between the bitumen droplets, which may be understood in terms of the interfacial visco-elastic behaviour and interfacial forces. The presence of air in the froth layer is a complicating factor.

**Froth treatment:** Most of the water and solids from the combined froths from the extraction processes must be removed before the bitumen is suitable for upgrading to synthetic crude oil. Gravity separation is ineffective, because there is very little density difference between the water and bitumen in the temperature range of 10 to 90°C. On an industrial scale, the froth is diluted with solvent, which reduces the density and viscosity of the bitumen phase. Water and solids are then removable



by gravity or centrifugal sedimentation. Chemical demulsifiers benefit these separation processes and may act by controlling the phase inversion that occurs in the centrifuges (Tyerman, 1989).

From a colloid science perspective, the interesting processes include (a) froth-naphtha mixing, where it is desirable to obtain a homogeneous naphtha-bitumen mixture, without breaking up the water droplets or transferring water-wet solids into the bitumen-naphtha phase, (b) coalescence of water droplets, to enhance separation rates, (c) the possible formation of structures due to agglomeration of bitumen, water, and solids which may be lost to tailings, carry excessive quantities of water and solids into the product, or persist as interfacial material between the bitumen-continuous and water-continuous regions. There are difficulties in studying the dewatering of froth since properties such as water droplet size in the diluted froth or diluted bitumen cannot be measured because these streams are quite labile and often separate into layers soon after samples are taken from the plant. An additional complication is that in the commercial operation, demulsifiers are added to aid the dewatering process. The exact mechanisms by which they act have not been established with any certainty.

## **SOME KEY PHYSICAL PROPERTIES**

**Viscosity:** Viscosity is most usefully expressed in quantitative terms. Consider two parallel plates of area  $A$  with a fluid sandwiched between them. If we maintain the parallel orientation between the plates, but displace one of the plates with respect to the other using a force,  $F$ , then a velocity gradient,  $dv/dz$ , is created within the fluid. The viscosity,  $\eta$ , is defined as the coefficient of the velocity gradient

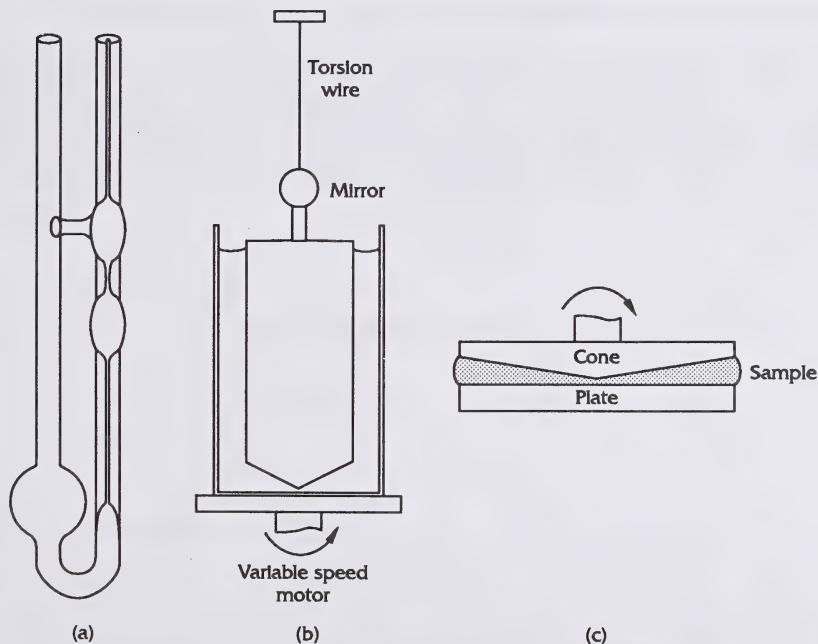
$$(4.2) \quad \frac{F}{A} = \eta \frac{dv}{dz}$$

**Methods to determine viscosity:** The capillary viscometer, illustrated in Figure 4.1, offers an easy and fast method to determine viscosity. The time,  $t$ , for a fluid of viscosity  $\eta$  and density  $\rho$  to flow through a given section of a capillary is given by

$$(4.3) \quad \eta = k \rho t$$

where  $k$  is a constant for a particular geometry of the capillary. This constant can be evaluated by using a fluid of known viscosity and density. The major disadvantage of using the capillary viscometer is the linear variation in the shear rate across the diameter of the tube, a consequence of laminar flow of a fluid in a pipe. This makes it difficult to obtain meaningful results when the viscosity of the sample depends on the shear applied.

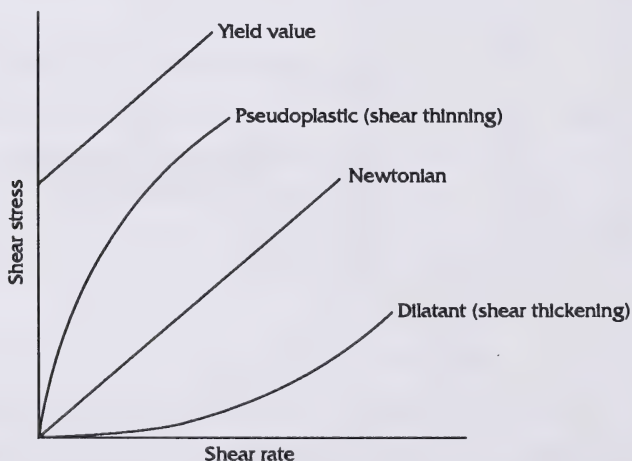
Rotational methods are commonly used to determine the viscosity when it is important to have a uniform shear field within the measuring volume. The most common geometries are shown in Figure 4.1. Shearing of the fluid is brought about



**Figure 4.1.** Schematic diagrams of a capillary viscometer (a), concentric cylinder (b) and cone and plate (c) equipment for determining viscosity.

by rotation of one of the elements with respect to the other. The stress response of the fluid is measured as a torque on the stationary element. In general, with a few specifications of geometry, the shear rate can be related to the rotational speed. Measurements are conducted by varying the rotational speed and measuring the stress response. Characteristic shear/stress responses are shown in Figure 4.2. A Newtonian system is defined as having a linear relationship between shear stress and shear rate (i.e., the viscosity is independent of the shear rate), and the slope of the straight line yields the viscosity, as defined in Eqn 4.2. Non-Newtonian behavior is a nonlinear relationship between shear stress and shear rate and can have several forms. Some of these are illustrated in Figure 4.2 and indicate that the viscosity can be strongly dependent on the shear rate applied. One of the advantages of using rotational methods to determine viscosity for processing applications is that the viscosity can be determined under a shear regime relevant to the process.

**Electric properties of the interface:** Interfacial charge can originate through a variety of mechanisms. For the interfaces that have an influence on the hot water process, the principal mechanisms are the ionization of a surface group or adsorption of surfactant from the bulk to the interface. The surfactants are thought to be anionic,



**Figure 4.2.** Comparison of shear/stress relationships for Newtonian and non-Newtonian systems.

mostly carboxylates with some sulfonates (Schramm and Smith, 1985), and thus most of the interfaces involved are negatively charged. This surface charge attracts an excess of ions of opposite charge (counter-ions) towards the interface. The volume concentration of ions of type  $i$ ,  $n_i$ , can be expressed by the Poisson-Boltzmann equation

$$(4.4) \quad n_i = n_{i0} \exp \left[ \frac{-z_i e \psi_o}{\epsilon k T} \right]$$

where  $n_{i0}$  is the number of ions per unit volume in the bulk,  $z_i$  is the valency of ion  $i$ ,  $e$  is the electronic charge,  $\psi_o$  is the surface potential,  $\epsilon$  is the permittivity of the medium (expressed as the dielectric constant of the medium multiplied by the permittivity of free space),  $k$  is the Boltzmann constant, and  $T$  is the absolute temperature. Thus the equation predicts the existence of an excess of counter-ions with respect to the co-ions in the vicinity of a charged interface. The ion "layer" is known as the diffuse layer. The Gouy-Chapman model describes the potential distribution within this ion layer (Shaw, 1980). For the case of low surface potential, the potential,  $\psi$ , at a distance,  $x$ , from a surface of potential  $\psi_o$ , can be expressed by the equation

$$(4.5) \quad \psi = \psi_o \exp (-\kappa x)$$

where

$$(4.6) \quad \kappa = \left[ \frac{e^2 \sum n_i z_i^2}{\epsilon k T} \right]^{1/2}$$

As expressed by Eqn 4.5, the potential decays exponentially with distance from the surface of the particle. The steepness of the exponential decay of the potential is dependent on the factor  $\kappa$ , which is proportional to the concentration of electrolyte and valency of the counter-ion.  $\kappa$  is known as the Debye-Huckel reciprocal double layer thickness, and the value of  $1/\kappa$  approximates the "thickness" of the double layer.



As two similar surfaces approach one another, their ion layers will begin to overlap, resulting in coulombic repulsion. The approach of the well known DLVO theory (Verwey and Overbeek, 1948) is to calculate the electrostatic double layer interaction as well as the van der Waals interaction between the surfaces. The energy (or force) is then calculated as a function of distance of separation between the surfaces. Interpretation of the energy diagram leads to a prediction as to whether the surfaces will repel or attract each other. This particular theory has a wide variety of applications, including emulsion stability, separation of bitumen from a mineral surface, wetting characteristics, and flotation efficiency. One of the limitations of the theory is that there are many other interactions that are not considered. The influence of interfacial charge, however, can still be a dominating effect.

**Methods to investigate interfacial charge:** The most common method to obtain the electrokinetic potential of particles in emulsions and dispersions is electrophoresis. In this technique the dispersion is placed between two electrodes to which a potential is applied. If the particles possess charge, they migrate toward the electrode of opposite polarity with a velocity,  $v$ . The measured velocity divided by the strength of the electric field is known as the electrophoretic mobility,  $U$ . This experimental parameter is related to the zeta potential,  $\zeta$ , by

$$(4.7) \quad U = \frac{e\zeta}{\eta} \quad \kappa a \ll 1$$

and

$$(4.8) \quad U = \frac{2e\zeta}{3\eta} \quad \kappa a \gg 100$$

in which "a" represents the radius of the particle, and  $\kappa$  is the Debye-Huckel parameter, as defined in Eqn 4.6. The selection of the appropriate equation is governed by the parameter  $\kappa a$ , which expresses the thickness of the double layer in relation to the size of the particle. Eqn 4.7 is known as the Huckel equation and was derived with the assumption that the particle was a point charge. Eqn 4.8 is known as the Smoluchowski equation and treats the particle as an infinitely large charged surface. Thus, calculation of the zeta potential from the measured electrophoretic

mobility requires knowledge of the concentration of electrolyte and size of the particle. The general theoretical relationship between zeta potential, electrophoretic mobility, and the parameter  $\kappa a$  is complex and has been developed by O'Brien and White (1978). It has been widely used but still awaits experimental verification for an adequately wide range of zeta potential. Fortunately, for most oil field applications the concentration of electrolyte in the aqueous phase is large enough that Eqn 4.8 can be used (Schramm, 1992).

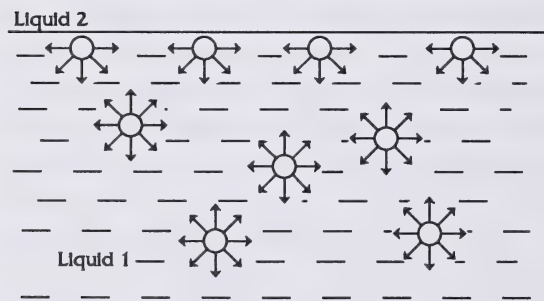
There are many instruments commercially available that enable the researcher to determine electrophoretic mobility. They differ in the method of measuring the velocity of the particles of the dispersed phase. In one method, the velocity is measured by timing the movement of a particle over a grid of known spacing. Newer instruments determine the velocity from the Doppler frequency shift of scattered laser radiation. The advantage of using the latter type of instrument is that velocities of several thousand particles can be determined quickly in a single measurement and a distribution of mobilities can be obtained.

There are two other applicable methods that rely on different electrokinetic phenomena, which yield the same information as electrophoresis. They are the streaming potential and sedimentation potential methods. In electrophoresis, an electric potential is applied to the colloidal system and the velocity of the charged particle relative to the solution is measured. In the streaming potential method, a solution is made to flow over a charged surface resulting in a measurable potential difference. The charged surface (usually a capillary tube or porous plug) is stationary and movement of the fluid is induced by the application of pressure. The potential difference created is indicative of the zeta potential of the material in the capillary or the porous plug. The utility of this method is that it can be used for minerals that sediment quickly due to the large density difference between particle and suspending medium. In the rising (sedimentation) potential method, movement of the particle is induced by gravitational separation. This method has received little attention from researchers because of experimental difficulties with measuring the relatively small potentials involved (Hunter, 1981). It has been used, however, to evaluate the zeta potential of air bubbles (Usui and Sasaki, 1978).

Recently an electroacoustical instrument has appeared on the market. One of the advantages of this technique is that signals are acquired continuously and the

entire sample can be titrated as a function of pH, electrolyte concentration, or chemical addition. In one mode of operation an alternating electric field ( $\sim 1.0$  MHz) is applied to the sample. The particles of the dispersed phase vibrate at the same frequency as the applied field, with the amplitude of vibration proportional to the zeta potential and the size of the particle (Sawatzky and Babchin, 1992). The vibrating particles of the disperse phase produce a sonic field; the strength of this sonic field is measured with a pressure transducer. The zeta potential can then be calculated. This particular operation mode is called Electrokinetic Sonic Amplitude. In the converse mode of operation, a sonic field is applied to the colloid of interest. If there is a density difference between the particles of the dispersed phase and the suspending fluid, relative motion is created between the particle and its surrounding double layer. The result of this relative movement is a measurable potential. This mode is known as the Ultrasound Vibration Potential (UVP) and is valuable in the study of systems where the continuous phase has relatively low conductivity (e.g., oil). This technique is described in detail in a review article by Babchin et al. (1989).

**Interfacial tension:** In bulk solution, the molecules of a given compound are equally attracted in all directions by dispersion forces (see Figure 4.3). A molecule at



**Figure 4.3.** Schematic representation of the origin of interfacial tension. The molecules in the interior of the solution are attracted equally on all sides to other molecules. The molecules at the interface are attracted toward the interior of the solution, resulting in contraction of the interface.

the interface, however, is unequally attracted toward the bulk of the solution. This attraction from the surface toward the bulk tends to contract the interface and also results in a lower concentration of molecules at the interface. Additional attractive interactions between the molecules at the interface also tend to contract the size of the interface, contributing to the surface tension.

**Methods to investigate interfacial tension:** Methods to investigate interfacial and surface

tension can be divided into two categories: those which measure the force required to create new interfacial area and methods which measure the shape of a droplet under the influence of a known force. In the force measurement methods, the interface is deformed with an object of known size, and the amount of force required to deform the interface by that area is measured and the interfacial tension calculated. The Wilhelmy plate and the DuNouy ring techniques are two of the methods which fall into this category. These methods are especially applicable to determining the gas/liquid tension because the assumption that one of the fluids wets the material (i.e., zero contact angle) of which the object is constructed is more nearly valid for this application.

Perhaps the best method for determining aqueous/air surface tensions is the maximum bubble pressure technique. This technique measures the pressure difference,  $\Delta P$ , between two gas bubbles formed at the tips of two capillaries of radii  $r_1$  and  $r_2$ . The relationship between the pressure difference and the surface tension is expressed by the Young-Laplace equation

$$(4.9) \quad \Delta P = \gamma \left[ \frac{1}{r_1} + \frac{1}{r_2} \right]$$

where  $\gamma$  is the surface tension. This technique has been used to monitor surface tension when determining surfactant concentration by titration (Schramm, Smith, and Stone, 1984). Additional information can be obtained from this technique by varying the bubble rate, which yields a dynamic surface tension.

The so-called drop volume method is a combination of force and shape methods. In this method the weight of a droplet that detaches from the tip of a capillary is measured. Through knowledge of the density, the volume may be calculated. It is assumed that the gravitational force acting on the droplet is balanced by the interfacial tension. The advantage of using this method is that results are obtained quickly and with a minimum amount of instrumentation. The disadvantages of using this method are discussed clearly by Heimenz (1977).

The spinning drop method can be used to determine interfacial tensions. In this method a droplet of material is made to deform as the tube that it is contained within is spun in a radial direction. The force that is applied to the droplet can be



related to the rotational speed of the tube. The shape of the droplet is determined as a function of rotational speed, and the interfacial tension can be calculated. A difficulty in using this technique with the bitumen-water system is the small and uncertain density difference; this can be avoided by use of  $D_2O$  in place of water (Takamura and Isaacs, 1989). This method is best suited for systems that have low interfacial tension.

In the pendant or sessile drop methods the shape of a droplet of known volume is measured accurately. Previously, this was achieved by tedious measurements using a microscope, which severely limited the speed of the technique. The technological advances in modern video recording and computational facilities make profile fitting of pendant or sessile droplets an efficient and accurate method for measuring either interfacial tension or contact angle (Boyce et al., 1984; Jennings and Pallas, 1988). With the high speed at which profiles can be acquired and analyzed, the method is readily adaptable to systems having time dependent interfacial tension or contact angle.

## **THE PHYSICAL CHEMISTRY OF OIL SAND CONDITIONING**

**Bitumen/water interfacial charge:** It is known that the repulsive interaction between the negatively charged bitumen and negatively charged sand grains is the main driving force in the initial separation of the bitumen from the mineral matrix (Takamura and Chow, 1983; Schramm and Smith, 1985). Therefore, it is useful to change the chemistry of the process to increase the negative charge of each of these two interfaces and thereby increase the separation efficiency. In commercial practice this is achieved by the addition of NaOH.

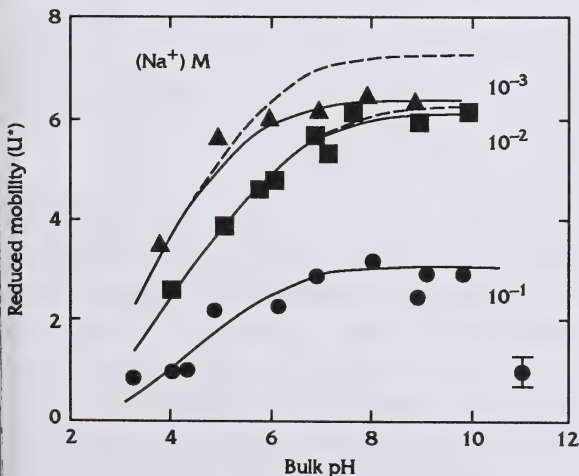
Two studies have been carried out that considered the mechanisms by which the charge at the bitumen/water interface originates. It was assumed in both studies that the natural surfactants present in bitumen are responsible for the charge, but that the exact mechanism of charging differs. In the first study, Takamura and Chow (1985) proposed that the ionization of the surfactants at the interface leads to the surface charge. In that study theoretical expressions were developed using the Ionizable Surface-Group Model (Healy and White, 1978) that permitted the calculation of the electric properties of the interface as a function of solution pH and

sodium ion concentration. The results are shown in Figure 4.4, where the measured reduced electrophoretic mobilities (symbols) are compared to the results of the model calculation (curves). Reduced (or dimensionless) electrophoretic mobilities,  $U^*$ , are related to the electrophoretic mobility,  $U$ , by the relationship

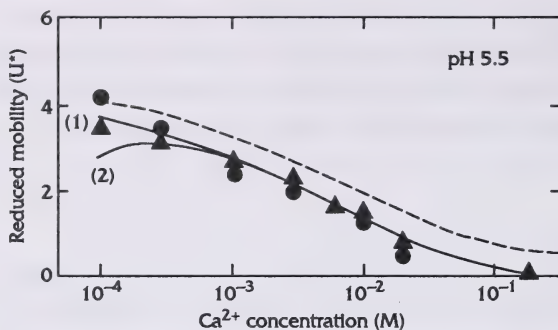
$$(4.10) \quad U^* = \frac{3 e \eta |U|}{2 \epsilon k T}$$

Excellent agreement between the measured mobilities and those calculated using the model was obtained over a wide range of solution pH and sodium ion concentration. For a constant sodium ion concentration Figure 4.4 shows the increase in mobility with increasing solution pH. As reported in an earlier work (Takamura and Chow, 1983), the increase in recovery in the extraction process with the addition of caustic could be partially explained by the increase of charge at the bitumen/water interface with increasing solution pH.

In an extension of the charge modelling work, Chow and Takamura (1988) addressed the influence of the presence of calcium ions. In the presence of this divalent ion, the charge at the bitumen/water interface was reduced to a greater extent than predicted by the influence of the increase in ionic strength (Figure 4.5). This was explained in that study by invoking a specific interaction between calcium ions and



**Figure 4.4.** Measured (symbols) and calculated (curves) electrophoretic mobilities for Athabasca bitumen droplets in water as a function of pH in  $10^{-3}$ ,  $10^{-2}$ ,  $10^{-1}$  M NaCl. The error bar at the lower right indicates the reproducibility of a measured mobility. From Chow and Takamura (1988).



**Figure 4.5.** Measured (symbols) and calculated (curves) electrophoretic mobilities of the Athabasca bitumen droplets in water in the absence (●) and presence (▲) of  $10^{-2}$  M NaCl as a function of  $\text{Ca}^{2+}$  concentration. The dashed curve represents the prediction of the model without any interaction between the calcium ion and the surface group. When ion binding is included (solid curves), better agreement is achieved. From Chow and Takamura (1988).

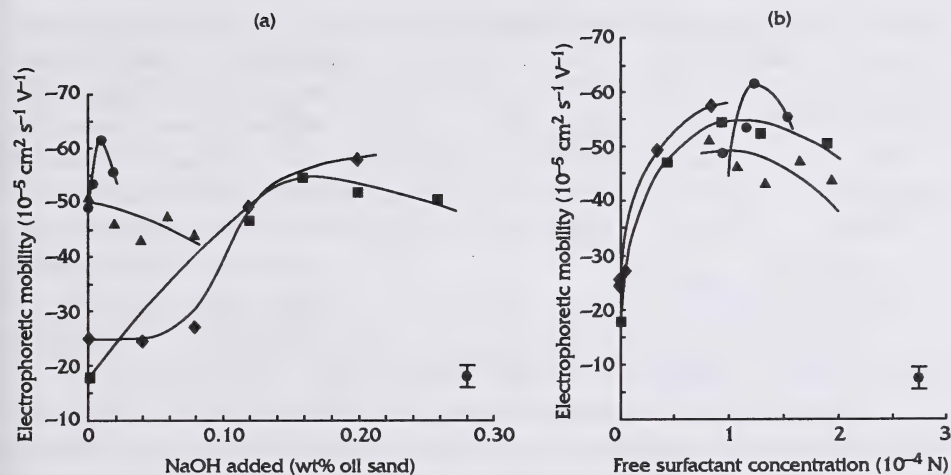
the surface groups. As shown in Figure 4.5, satisfactory agreement between the prediction of the Ionizable Surface-Group Model and measured electrophoretic mobilities was obtained when a binding constant between the ionized surface group and the calcium ion was invoked.

In the other study, Schramm and Smith (1985) measured the electrophoretic mobilities of bitumen droplets that were recovered during laboratory batch extraction unit (BEU) experiments. The results are shown in Figure 4.6a where the electrophoretic mobility is plotted as a function of the NaOH added during the

extraction experiment. The authors found a strong correlation between the carboxylate surfactant concentration in the aqueous phase and the electrophoretic mobility of the bitumen droplets (Figure 4.6b), and postulated that a critical ionized surfactant concentration was required to achieve maximum recovery.

Tyerman and Smith (1990) developed a simple physical model relating the surface charge to adsorption of the ionized surfactant and allowed for screening of this charge by the electrolytes. The electrophoretic mobilities,  $U$ , for bitumen droplets, fine particles, and bubbles from nearly two hundred batch extractions were found to follow linear expressions of the form

$$(4.11) \quad \kappa U = -A_0 - A_1 C_c - A_2 C_s$$



**Figure 4.6.** Electrophoretic mobilities of bitumen droplets, from process extracts, measured as a function of NaOH added (expressed as wt% of oil sand) during processing (a) and as a function of the free surfactant concentration (b). Experiments were conducted with rich ( $\bullet$ ), average ( $\blacktriangle$ ), lean ( $\blacklozenge$ ), and a mixture of average and lean ( $\blacksquare$ ) oil sands. From Schramm and Smith (1985).

where  $C_c$  and  $C_s$  were defined as the “activity” of the carboxylate and sulfonate surfactant, respectively, and  $\kappa$  is given by Eqn 4.6. The “activity” of a particular surfactant was defined as the square root of the product of the concentration of the ionized surfactant and the concentration of the counter ions. The statistically fitted values of  $A_0$ ,  $A_1$ , and  $A_2$  for bitumen droplets, solid particles, and air bubbles are given in Table 4.1. The model accounts quantitatively for the minimum (most negative) electrophoretic mobilities as shown in Figure 4.6. Caustic addition increases the ionic strength as well as the surfactant activity, so that the increased surface charge is increasingly screened by the electrolytes. It was suggested that the same opposing effects also contribute to the development of the maximum processibility. The conclusions drawn from this correlation were: (i) counter-ions are important in determining surfactant adsorption, (ii) only about 75% of the surface charge is due to surfactant adsorption, and (iii) the charges at the bitumen/water, solid/water, and air/water interfaces are coupled via the dissolved surfactants and do not arise independently by ionization of different surface species at these interfaces.



**Table 4.1.** Coefficients<sup>1</sup> for correlation of electrophoretic mobilities

Dispersed Phase	$A_0$	$A_1$	$A_3$
Solids	4.02	0.0098	0.0014
Bitumen	4.63	0.0136	0.0022
Bubbles	4.48	0.0121	0.0031

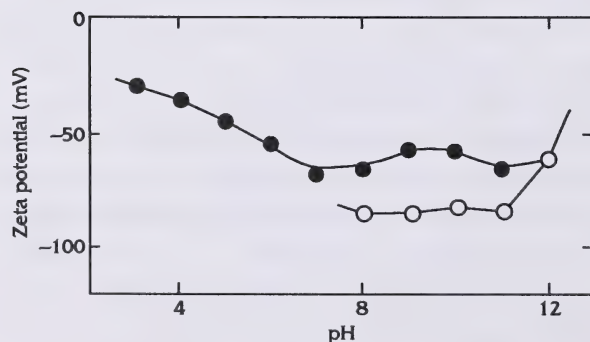
<sup>1</sup> as shown in Eqn 4.11.

From Tyerman and Smith (1990)

In summary, the two proposed models for the origin of the charge at the bitumen/water interface are (a) the ionization of natural surfactants at the bitumen/water interface and (b) extraction of surfactants or their precursors from the bitumen and their adsorption

not only at the bitumen/water interface, but also at the other available interfaces.

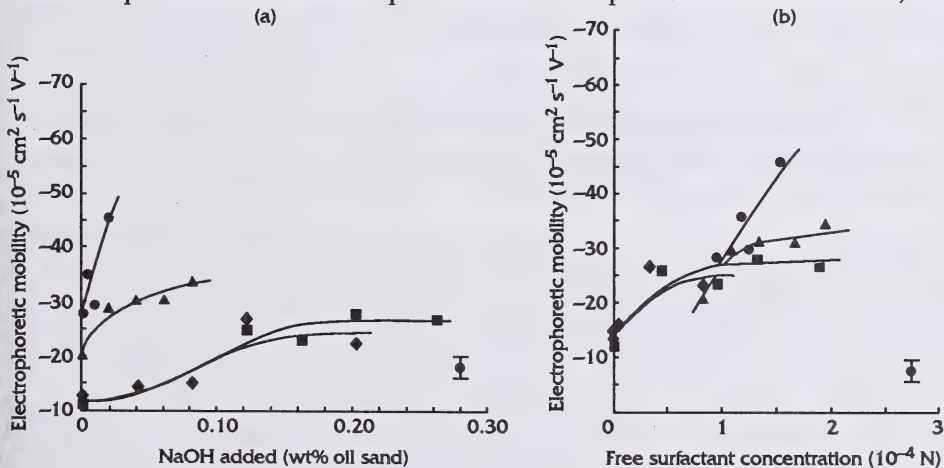
**Charge at the mineral/water interface:** Previous studies (Takamura and Chow, 1983), have shown that the charge characteristics of the solid/water interface can influence the initial separation of bitumen from the sand grains. The solids in the Athabasca deposit consist mainly of quartz (85%) and clays which are primarily kaolinite and illite, with smaller amounts of montmorillonite and other fines. The charge characteristics of the pure minerals have been investigated in a large number of studies, but the electric properties of the fine solids separated from oil sand have received less attention. The zeta potentials, calculated from measured electrophoretic mobilities, of solvent extracted oil sand solids as a function of pH and sodium and calcium ion concentrations are shown in Figure 4.7 (Takamura and Chow, 1983). A weakness of this analysis is that the possible influence that the natural surfactants



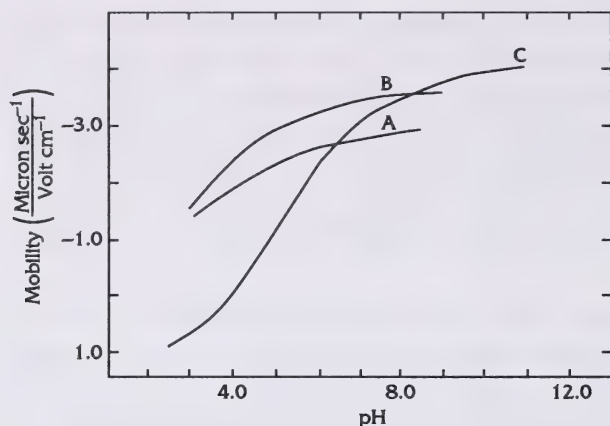
**Figure 4.7.** Zeta potentials of solvent extracted sand from Athabasca oil sand calculated from measured electrophoretic mobilities as a function of solution pH. Open symbols refer to various  $\text{Na}^+$  concentrations while solid symbols refer to constant  $\text{Na}^+$  concentration of  $10^{-2}$  M. From Takamura and Chow (1983).

may have on the charge characteristics of fines was not considered. It is known that the adsorption of surfactant can modify the charge at the solid/water interface. The influence of the adsorption of natural surfactant on the electrophoretic mobility of the solids was shown by Schramm and Smith (1985) in the same series of experiments as for bitumen droplets; good correlation was achieved between the free surfactant concentration and electrophoretic mobility of the solids. These are shown in Figure 4.8. The coefficients for the mobility of solids as expressed by Eqn 4.11 are given in Table 4.1.

Some evidence that natural surfactants from the bitumen adsorb onto the solids and modify the interfacial charge had been reported by researchers investigating the electric properties of the solids within the tailings (Srinivasan, et al., 1982; Chow and Burgess, 1989). Figure 4.9 shows the electrophoretic mobilities of kaolinite as a function of solution pH in diluted pond water, kaolinite in an aqueous solution equivalent to the diluted pond water in ion species and concentrations, and



**Figure 4.8.** Electrophoretic mobilities of fine minerals from the batch unit extraction unit, measured as a function of NaOH added (expressed as wt% of oil sand) during processing (a) and as a function of the free surfactant concentration (b). Experiments were conducted with rich (●), average (▲), lean (◆), and a mixture of average and lean (■) oil sands. From Schramm and Smith (1985).



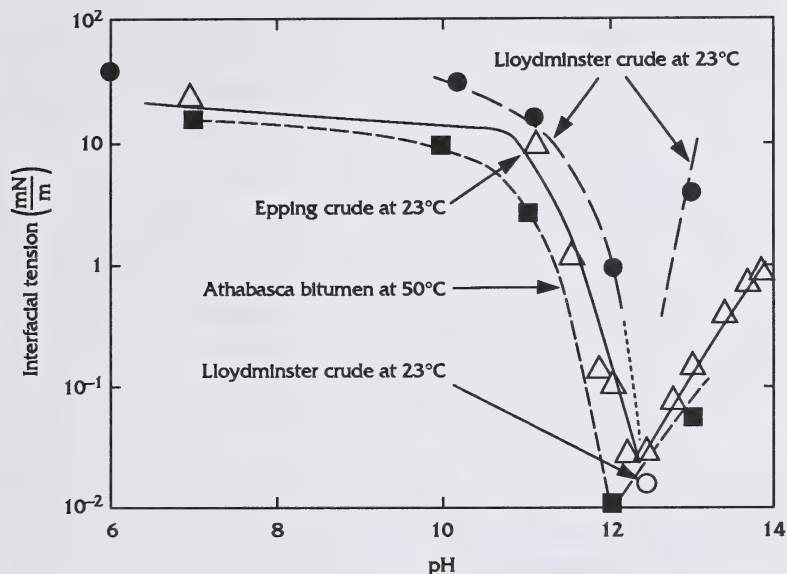
**Figure 4.9.** Electrophoretic mobilities of  $\text{Na}^+$  kaolinite as a function of solution pH in diluted tailings water (A), in “synthetic tailings water” (B), and in water with an equivalent  $\text{Na}^+$  ion concentration of  $10^{-4}$  M (C). The change in mobility when the kaolinite was immersed in water that was exposed to bitumen is indicative of adsorption from solution. From Srinivasan et al. (1982).

kaolinite in “synthetic pond water.” “Synthetic pond water” was defined as water that is similar to pond water in ion species and concentration and that had also been exposed to bitumen. It is clear from the figure that some adsorption from solution is occurring and that such adsorption is modifying the electric properties of the surface.

**Bitumen/water interfacial tension:** It is thought that the bitumen in oil sands exists as an oil-continuous film that fills the pores in the mineral matrix (see Chapter 1). A thin film of water (~10 nm) separates

the bitumen from physical contact with the minerals. As the bitumen is displaced from the mineral matrix, the interfacial area between bitumen and water decreases. This process is favored by a high interfacial tension. The bitumen/water interfacial tension as a function of solution pH is shown in Figure 4.10. This figure illustrates the dramatic decrease in interfacial tension as the solution pH changes from 9.0 to 11.0. Thus, the addition of caustic to increase the repulsion between the bitumen and the mineral matrix to enhance the separation will actually begin to hinder separation at too high a pH because of the reduction in interfacial tension driving force. The addition of caustic also has benefits for the flotation step (see section on flotation).

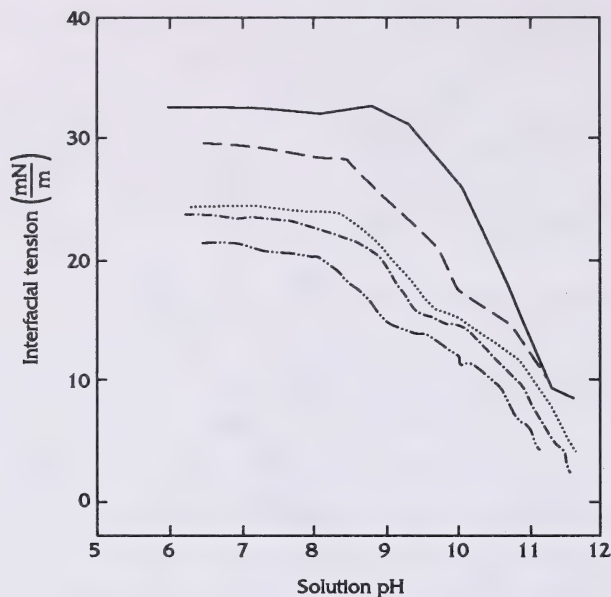
Presumably, the reduction of interfacial tension between bitumen and water with increasing solution pH is due to ionization of the natural surfactants present in the bitumen. In a series of experiments, Dobrogowska and Hepler (unpublished)



**Figure 4.10.** The influence of solution pH on the interfacial tension between heavy water and Athabasca bitumen, Epping crude, and Lloydminster crude. From Isaacs and Morrison (1985).

examined the interfacial tensions of an organic phase and aqueous solutions. The organic phase was 5% bitumen dissolved in toluene. The bitumen was toluene extracted Athabasca bitumen or coker feed bitumen from the Syncrude commercial operation. Experiments were conducted as a function of solution pH and as a function of time of oxidation with air at room temperature for periods of up to 15 weeks. The results are shown in Figure 4.11 where the interfacial tensions are plotted as a function of solution pH. Several trends are apparent from the figure. All the curves show a striking decrease in interfacial tension with increasing solution pH, similar to that observed for bitumen (Figure 4.10). The curves for the coker feed bitumen show a decrease in interfacial tension with increasing time of oxidation. This agrees with the results of Isaacs and Morrison (1985) who observed an interfacial film that formed on pendant droplets of bitumen in water. It was found that the film showed an enhanced concentration of carboxylate groups at the bitumen/water interface. Photo-oxidation was the suspected cause as bitumen droplets kept in the dark did not show

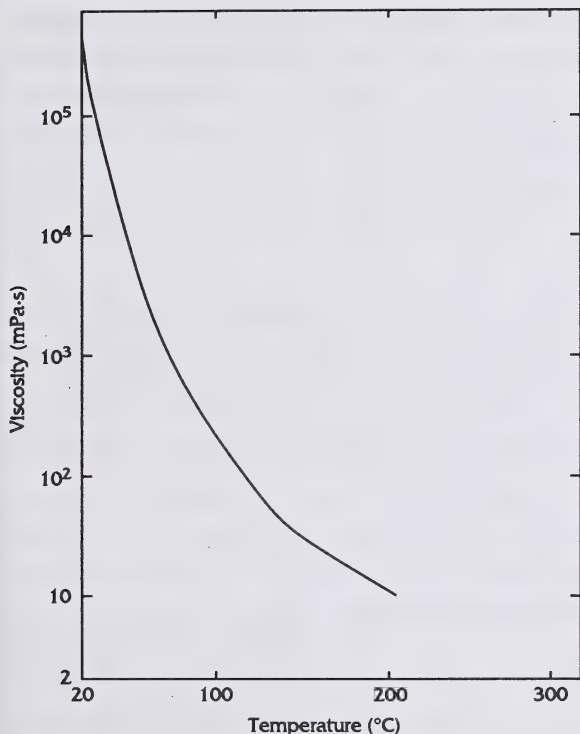




**Figure 4.11.** The interfacial tension between water and a solution of solvent extracted bitumen (—), and coker feed bitumen (---), dissolved in toluene as a function of solution pH. Additional experiments were conducted in which interfacial tension was measured as a function of time of exposure to gentle oxidizing conditions. Measurements at 0 (---), 4 weeks (....), 6 weeks (— · —), and 15 weeks (— · · —). From Dobrogowska and Hepler.

the filming process. The oxidized droplet also exhibited a change in shape to a form that suggested a decrease in interfacial tension. Another interesting observation from Figure 4.11 is that the coker feed bitumen shows slightly higher concentrations of surface active components (i.e., lower interfacial tension) than solvent extracted bitumen. The reason for this is not known at this time.

**Viscosity of bitumen:** The previous sections described the charge at the bitumen/water and mineral/water interfaces as well as interfacial tension as the driving forces for the separation of the bitumen from the sand grains. These are resisted by the viscous drag of the bitumen (Takamura and Chow, 1983). The viscosity of Athabasca bitumen as a function of temperature is shown in Figure 4.12 (Seyer and Gyte, 1989; also see Chapter 1, and Appendix 1). The significant reduction in viscosity of bitumen with increases in temperature is the reason why the two successful commercial processes are operated at elevated temperature.



**Figure 4.12.** The mean viscosity of Athabasca bitumen as a function of temperature. From Seyer and Gyte (1989).

$$(4.12) \quad m = \frac{4 \pi \epsilon \zeta_p \zeta_b}{kA}$$

where  $\zeta_p$  and  $\zeta_b$  are the zeta potentials of the particle and air bubble, respectively,  $A$  is the Hamaker constant for the bubble and oil droplet immersed in water, and  $\kappa$  is defined as in Eqn 4.6. A theoretical value of  $m$ , above which the flotation efficiency was drastically reduced, was estimated using DLVO theory. The criterion for this value was a zero interaction energy (i.e.,  $F_T = 0$ ) between the air bubble and oil

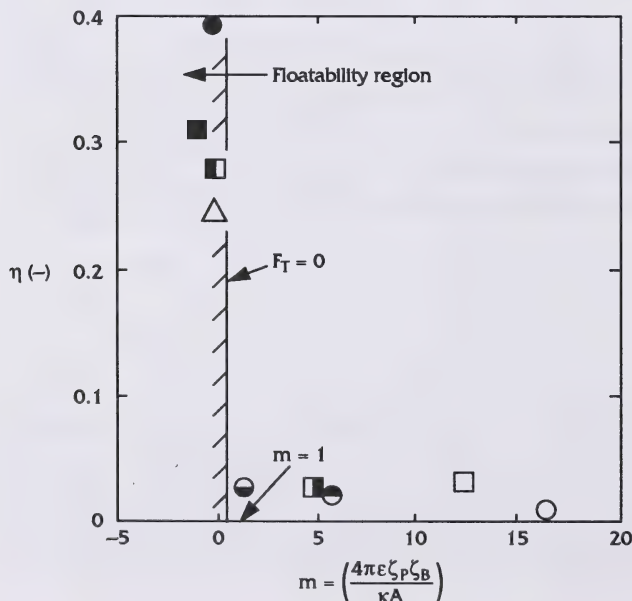
## THE PHYSICAL CHEMISTRY OF BITUMEN FLOTATION

**Charge at the water/air interface:** Although the charge at the water/air interface is not generally thought to play a large role in the attachment of air bubbles to the bitumen droplets, there has been some evidence in the literature that the maximum recovery of oil in a flotation process from an oil-in-water emulsion was dependent not only on the zeta potential of the oil droplets but also on the zeta potential of the air bubbles (Okada et al., 1990). In that paper the fraction of solids that was removed by flotation was termed the flotation efficiency,  $\eta(-)$ , and was shown to correlate to a parameter  $m$

droplet. The result of the calculation was a critical value of  $m$  equal to 0.31, which is in good agreement with the experimental results (Figure 4.13). Using the correlation expressed by Eqn 4.11 to estimate electrophoretic mobilities of air bubbles and hence zeta potentials, values of  $m$  were calculated (Tyerman, 1990). The results showed that for conditions corresponding to conditioning or flotation stages, the value of  $m$  was at least an order of magnitude larger than the theoretical critical value, suggesting that other forces aid the attachment of bitumen to air, or that the conditions are far from equilibrium.

**Bitumen/water and water/air interfacial tensions:** Leja and Bowman (1968) considered the separation and flotation stages of the hot water process, using a theoretical analysis based on free energy changes of the interfaces involved. For the flotation stage, they considered two possibilities for the configuration of the aerated bitumen droplet. The first, contact attachment of the air bubble to the bitumen is described by the inequality

$$(4.13) \quad \gamma_{a/o} + \gamma_{o/w} > \gamma_{a/w}$$



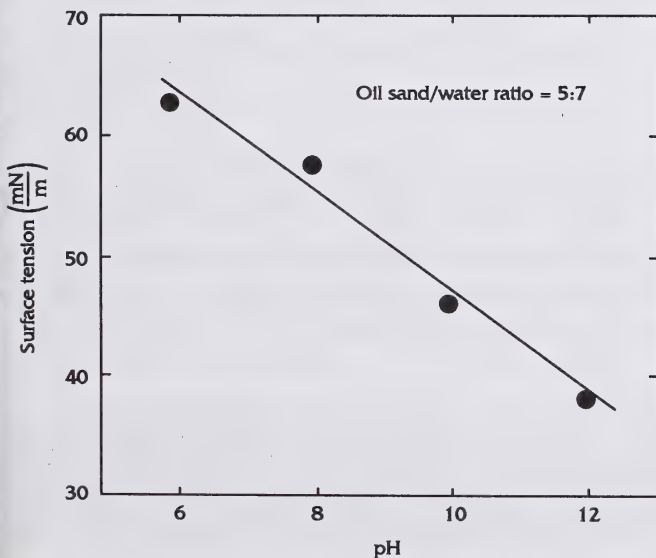
**Figure 4.13.** The fraction of material recovered by flotation,  $\eta(-)$ , as a function of the parameter  $m$  as expressed by Eqn 4.12. The vertical border defines the condition that the calculated force of interaction,  $F_T$ , between bubble and oil droplet is zero. The agreement between the observed and predicted recovery suggests that the zeta potentials of both the bubble and oil droplets were important to flotation processes. From Okada et al. (1990).

while the second, attachment and filming of the bitumen over the air droplet, is described by the inequality

$$(4.14) \quad \gamma_{a/o} + \gamma_{o/w} > \gamma_{a/w}$$

where  $\gamma_{a/w}$ ,  $\gamma_{o/w}$ , and  $\gamma_{a/o}$  are the air/water, oil/water, and air/oil interfacial tensions, respectively. In the case of the hot water process, attachment and filming is favored over contact attachment because the air/water tension,  $\gamma_{a/w}$ , is larger than the oil/water and air/oil interfacial tensions. Attachment and filming of the bitumen over air droplets was observed through a series of experiments (Bowman, 1969) where aerated bitumen droplets were removed from the primary separation vessel and examined microscopically.

Figure 4.14 shows the data of Bowman (1967) where the surface tension of a water-oil sand slurry was measured as a function of pH of the solution. The decline in the surface tension with increasing pH is presumably due to the ionization of the natural surfactants. In an attempt to improve understanding of the action of the surfactants, Tyerman (1989) systematically determined the surface tensions of aqueous



**Figure 4.14.** The surface tension of aqueous oil sand slurry as a function of solution pH. The decrease in surface tension with increasing solution pH is presumably due to the ionization of the natural surfactants present in the bitumen. From Bowman (1967).

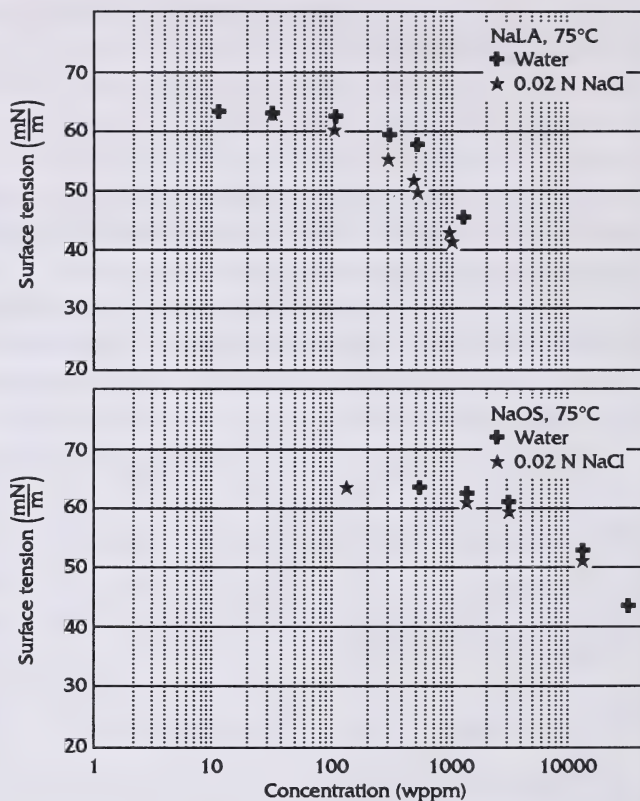


solutions of pure surfactant analogs of the natural surfactants. The surfactants used as analogs were sodium octyl sulfonate and sodium laurate. Investigations were conducted as a function of surfactant concentration, ionic strength, temperature, and the presence of divalent cation. At the concentrations of natural surfactants in the process (approximately 40 ppm in the middlings and 300 ppm in the slurry) the model compounds did not show significant reductions in surface tension at 75°C (see Figure 4.15). The presence of a small amount of divalent cation, however, had a significant effect (Figure 4.16).

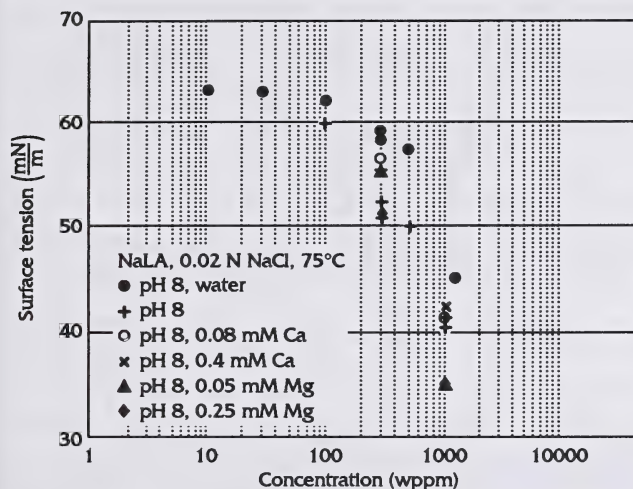
#### Fine solids as surface active agents:

The surface tension of a solid-in-water dispersion

can differ from that of pure water. This was shown for aqueous dispersions of kaolinite and montmorillonite by Schramm and Hepler (1992). When surface tension was determined using the DuNouy ring method, increases in surface tension were observed in the presence of the montmorillonite but not in the presence of kaolinite



**Figure 4.15.** The measured surface tension of water as a function of concentration of surfactant, expressed as weight parts per million (wppm). Shown here for sodium laurate (NaLA) and sodium octyl sulfonate (NaOS). Measurements were conducted at 75°C. From Tyerman (1989).



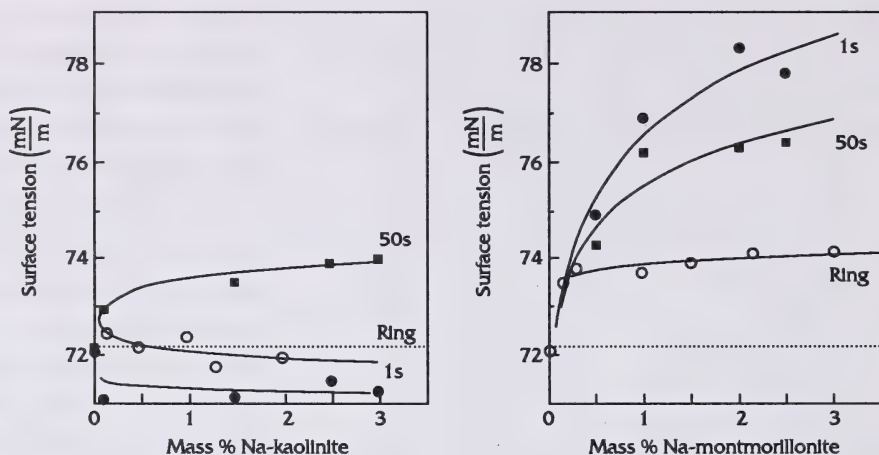
**Figure 4.16.** The effect of the presence of divalent ions on the measured surface tensions of aqueous solutions of sodium laurate (NaLA). Concentration of surfactant expressed as weight parts per million (wppm). The presence of the divalent ions at 1000 wppm NaLA significantly depresses the surface tension. From Tyerman (1989).

largest change in interfacial tension. The magnitudes of the changes are relatively minor, compared to the influence of the natural surfactants (see Figure 4.14).

The influence of clays in the water on the interfacial tension between toluene and water was also investigated by Schramm and Hepler. The results are shown in Table 4.2. Kaolinite in the water slightly decreased the interfacial tension while montmorillonite slightly increased the interfacial tension.

Levine and Sanford (1985) have discussed the stabilization of oil sand dispersions by fine solids having both water-wet and oil-wet regions on their surfaces. These "bi-wet" solids tended to gather at the oil/water interface and were considered to be "surface active." Their presence would change the measured

(Figure 4.17). Interesting results were observed when the maximum bubble pressure method was used to determine surface tension. Using this technique, the surface tension of the suspension was found to be dependent on the age of the surface, which was correlated with the bubble rate. For suspensions of kaolinite, the surface tension was lower at fast bubble rate (short surface age) and larger surface tension was observed with slower bubble rate (longer surface age) (Figure 4.17). For suspensions of montmorillonite, the fastest bubble rate led to the



**Figure 4.17.** The surface tensions of suspensions of kaolinite and montmorillonite in water, measured by the DuNouy ring method (open symbols) and the maximum bubble pressure method (full symbols) at different bubble rates. From Schramm and Hepler.

**Table 4.2.** Clay-in-water/toluene interfacial tensions<sup>1</sup>

Mass % kaolinite in water <sup>2</sup>	Water/toluene interfacial tension (mN/m)	Mass % montmorillonite in water <sup>3</sup>	Water/toluene interfacial tension (mN/m)
0	34.1	0	36.0
0.13	35.5	0.15	37.3
0.47	34.3	0.30	39.5
1.00	33.9	0.98	39.0
1.30	33.8	1.49	38.8
2.00	32.3	2.14	39.1
		3.00	39.5

<sup>1</sup> temperature was 24.5°C

<sup>2</sup> water contained 0.01 mol/L NaOH

<sup>3</sup> suspension pH was between 9.2 and 9.6

From Schramm and Hepler (1992)

oil/water interfacial tension, and can be expected to alter the interfacial rheology as well as the forces between approaching oil droplets whose surfaces are coated with solids. All these factors can affect coalescence rates and bitumen aeration.

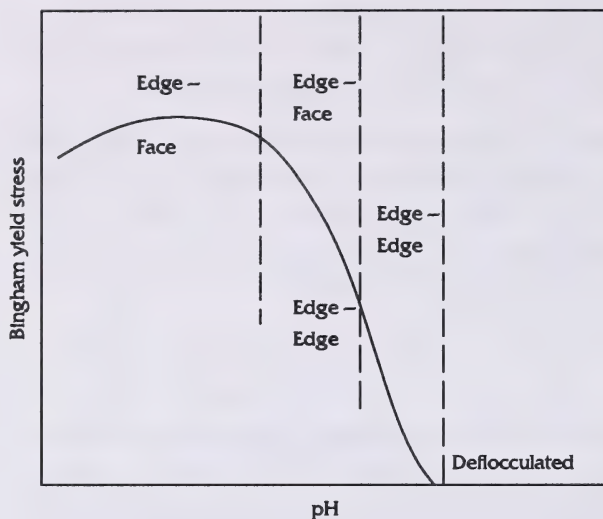
**Viscosities of suspensions:** In the primary separation vessel, the aerated bitumen droplets rise through a complex suspension of dispersed oil and mineral matter. Thus, the viscosity of the suspension rather than the viscosity of the continuous phase becomes important. For dilute (volume fraction  $\phi < 0.1$ ) suspensions, the viscosity can be represented by the equation

$$(4.15) \quad \frac{\eta}{\eta_0} = 1 + k_1\phi + k_2\phi^2$$

where  $\eta$  and  $\eta_0$  are the viscosities of the suspension and of the pure solvent, respectively,  $\phi$  is the volume fraction of dispersed phase, and  $k_1$  and  $k_2$  are constants. The Einstein equation was derived with the assumption that the particles were uncharged spheres, leading to the result  $k_1 = 2.5$ . Application of Eqn 4.15 to clay-in-water suspensions has shown the magnitudes of the constants depend on the actual shape of the particles, the interaction between the particles, and the particular species of clay (Kasperski et al., 1986).

For the clay species present in the formation, and at the concentrations of solids in the primary separation vessel (typically 10–15 wt%), it is likely that the interactions between the clay particles will have the greatest influence on the viscosity (Schramm, 1989). For kaolinite particles it has been reported (Rand and Mellon, 1978) that the viscosity is influenced by the state of dispersion. This is illustrated schematically in Figure 4.18 where the Bingham yield stress for a kaolinite suspension is shown as a function of pH of the solution. The state of dispersion of the kaolinite particles can be altered by changes in the pH of the solution. This was the primary concept followed by Takamura and Wallace (1988). In their study a model was developed that assumed that primary recovery in a laboratory batch extraction unit (BEU) could be correlated to the viscosity of the middlings and hence the state of dispersion (i.e., coagulated or stable) of the mineral matter. The predictions of stability were based on calculations using DLVO theory. It was assumed that the electric properties of the edges of the kaolinite particles determined the stability of the suspension and these were calculated using the Ionizable Surface-Group Model



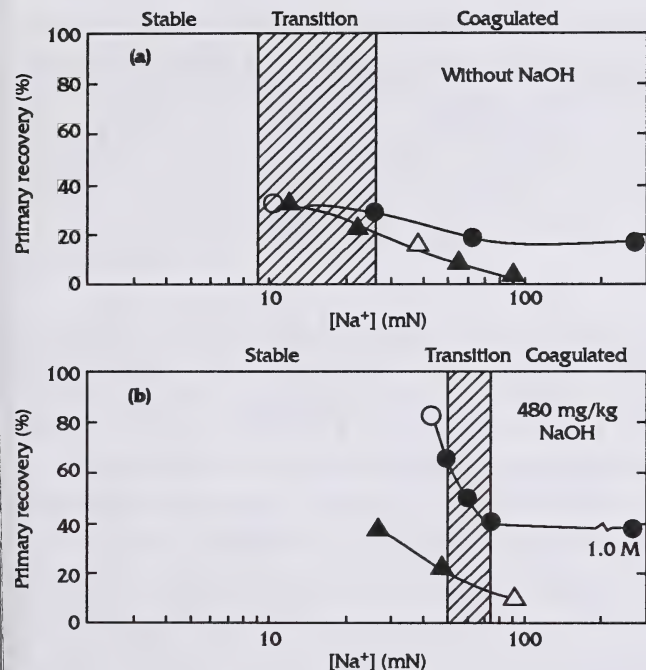


**Figure 4.18.** Interpretation of the effect of pH on the Bingham yield stress of kaolinite suspension in terms of particle interactions. From Rand and Mellon (1977).

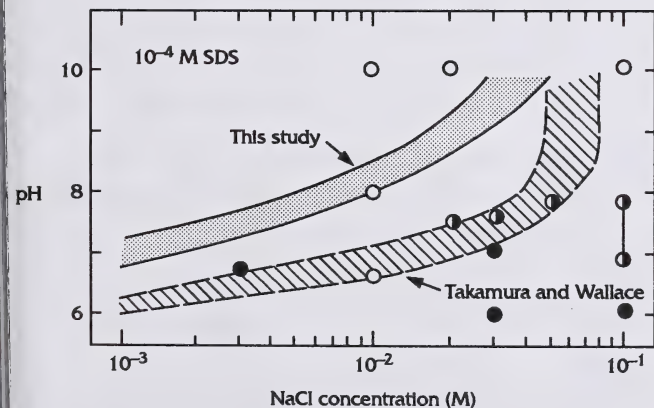
technique has been reported by Chow (1991). In that work it was shown that the measured stability for a sodium kaolinite suspension did not agree with the stability diagram reported by Takamura and Wallace (1988). The stability diagrams as reported by Takamura and Wallace and Chow are shown in Figure 4.20. The shaded zone in the figure represents the transition zone from a dispersed to coagulated state. When the measurements were conducted in the presence of a sulfonate surfactant (symbols in Figure 4.20), an increase in the stability of the dispersion was observed. The measured stability was then in agreement with results reported by Takamura and Wallace (1988).

(Healy and White, 1978). The calculations carried out were done as a function of sodium ion concentration and pH. Results were presented in terms of whether the mineral matter in the middlings was predicted to be coagulated, dispersed, or in transition. Good agreement between the calculated stability of the mineral matter and the percent recovery in the BEU was obtained (Figure 4.19). The role of natural surfactant was not considered in that study.

The stability of kaolinite measured directly using a light scattering



**Figure 4.19.** Comparison of the recovery of bitumen in the batch extraction unit for medium grade (circles) and low grade (triangles) oil sands as a function of sodium ion concentration. The figure has also been divided into zones that are the result of the calculated state of dispersion of the fine minerals in the middlings. This is shown for experiments with no caustic addition (a) and a caustic addition of 480 mg/kg oil sand (b). In general, primary recovery is reduced as the calculated state of dispersion of the minerals changes from a stable to coagulated regime. From Takamura and Wallace (1988).



**Figure 4.20.** Measured stabilities (symbols) of a kaolinite-in-water suspension as a function of pH and NaCl concentration in the presence of sulfonate surfactant (SDS). Open, half shaded, and full symbols refer to stable, weakly coagulated, and coagulated dispersion, respectively. The zone labelled as "This study" is the border between stable and coagulated in the absence of surfactant. The presence of the surfactant increases the zone of stability to match results of Takamura and Wallace (1988). From Chow (1991).

## THE PHYSICAL CHEMISTRY OF FROTH TREATMENT

**Solubilities and dissolution rates of bitumen in organic solvents:** Tyerman (1990) studied the rate and extent of dissolution of asphaltenes, maltenes, and whole bitumen into organic solvents. A spectrophotometric assay was used, based on the absorption of visible light at 405 nm (asphaltenes only) and 530 and 600 nm (both asphaltenes and maltenes). Mild agitation was applied at infrequent intervals, and the solubility of the various fractions of bitumen was determined 48 hours after the fraction of interest was mixed with the organic solvent.

According to this assay, the separated material labelled "maltenes" contained 3.7% asphaltenes. The asphaltene fraction showed a low solubility in naphtha, but the solubility progressively increased as the naphtha was pre-loaded with maltenes. A similar but smaller effect was noted with pentane as a solvent, which may explain why the separated maltenes retained some asphaltenes. The ratio of asphaltenes to maltenes in the naphtha solution was similar to their ratio in whole bitumen, suggesting that the asphaltenes are close to saturation in bitumen/naphtha solutions.

Dissolution rates under quiescent conditions were measured, after solvent was carefully deposited on top of a layer of asphaltenes in a spectroscopic cell. Results (Table 4.3) were expressed as the mass of asphaltenes moving into the solvent or solution, per unit area in unit time. The asphaltenes dissolved into toluene or naphtha

**Table 4.3.** *Dissolution rates of asphaltenes into organic solvents at 20°C*

Solvent	Asphaltene g	Solvent g	Appearance rate of asphaltenes in supernatant g/(hour · m <sup>2</sup> )
Naphtha	0.002	2.2 <sup>1</sup>	0.3
Toluene	0.051	2.5 <sup>1</sup>	0.4
Naphtha	0.006	2.1	0.3
Maltenes <sup>2</sup>	0.005	2.2	0.3
Bitumen <sup>3</sup>	0.002	2.2	0.2

<sup>1</sup> estimated values

<sup>2</sup> 1.6 g/L maltenes in naphtha

<sup>3</sup> 0.012 g bitumen in naphtha  
From Tyerman (1990)

at nearly the same rate. The mass transfer rate was decreased when the solvent was pre-loaded with bitumen, suggesting that the presence of maltenes within the bitumen formed a barrier to the dissolution of the asphaltenes. This was not observed, however, when the solution was pre-loaded with maltenes. Similar experiments were conducted with whole bitumen, which dissolved four orders of magnitude more rapidly than asphaltenes into toluene or naphtha. This rate was consistent with results of dissolution experiments where a metal disk was painted with bitumen and spun in an organic solvent.

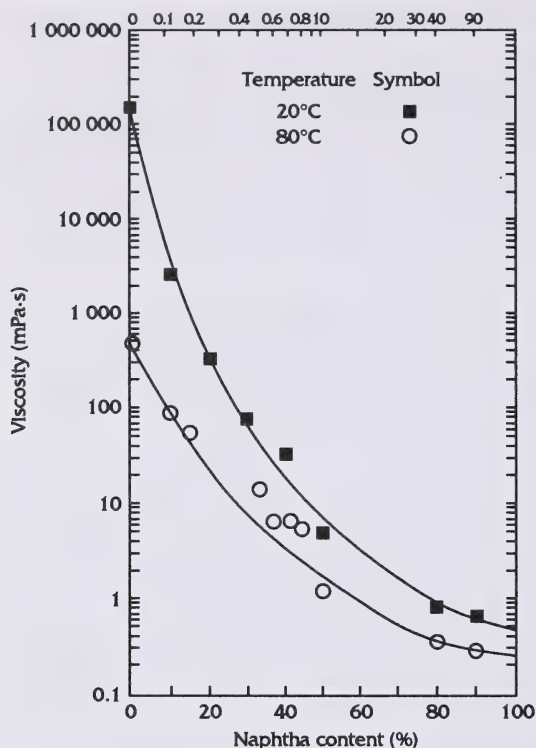
The observations in the dissolution rate experiments illustrate the strong affinity of maltenes for asphaltenes. There had been concern expressed in the industry that asphaltenes might be precipitated when froth was contacted with naphtha; results of these experiments suggest this is unlikely to occur.

**Viscosities of bitumen/solvent mixtures:** In the froth treatment stage of the extraction process, the froth is mixed with a nearly equal volume of diluent (naphtha) to reduce the viscosity and density of the oil phase and therefore hasten the sedimentation of the water droplets. The viscosities of mixtures of naphtha and bitumen were studied by Schramm and Kwak (1988). It was found that the viscosities of bitumen/naphtha mixtures were described adequately by the equations developed by Shu (1984). Figure 4.21 shows the measured values of the viscosity as a function of the naphtha content of the bitumen. The solid lines in the figure represent the prediction of the theory. In the same work, the viscosities of naphtha-diluted froth mixtures were determined. It was found that when the naphtha content was greater than 10 wt%, the viscosity of a froth/naphtha mixture could be predicted by the theoretical relationship for bitumen/naphtha mixtures.

**Bitumen/water interfacial tension:** Recent work (Isaacs et al., 1990) has shown the influence of the time dependent interfacial tension of the crude oil/water interface on the stability of water-in-oil emulsions. This information will aid in understanding the processes that occur during froth dewatering. A correlation was observed between the water recovered by centrifugation and the "spreading rate parameter" defined as

$$(4.16) \quad \text{spreading rate parameter} = \frac{\gamma_o - \gamma_t}{t}$$

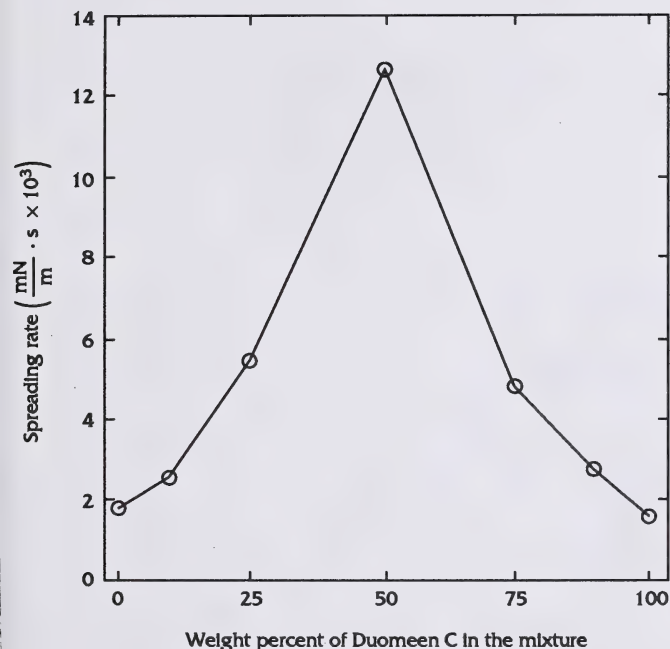




**Figure 4.21.** Viscosity as a function of naphtha content for bitumen/naphtha mixtures. Experimentally measured points (symbols) agree well with the calculated values from the Shu equations (curves). From Schramm and Kwak (1988).

Figure 4.24 shows the UVP signal as a function of time. At 8.0 minutes into the experiment the naphtha diluted froth was dosed with a demulsifier. The decrease in signal corresponded very well to an increase in the water droplet size as shown by the photo-micrographs. As in the previous study, excellent correspondence was achieved with the change in the UVP signal and the amount of water and solids released by centrifugation (Figure 4.25).

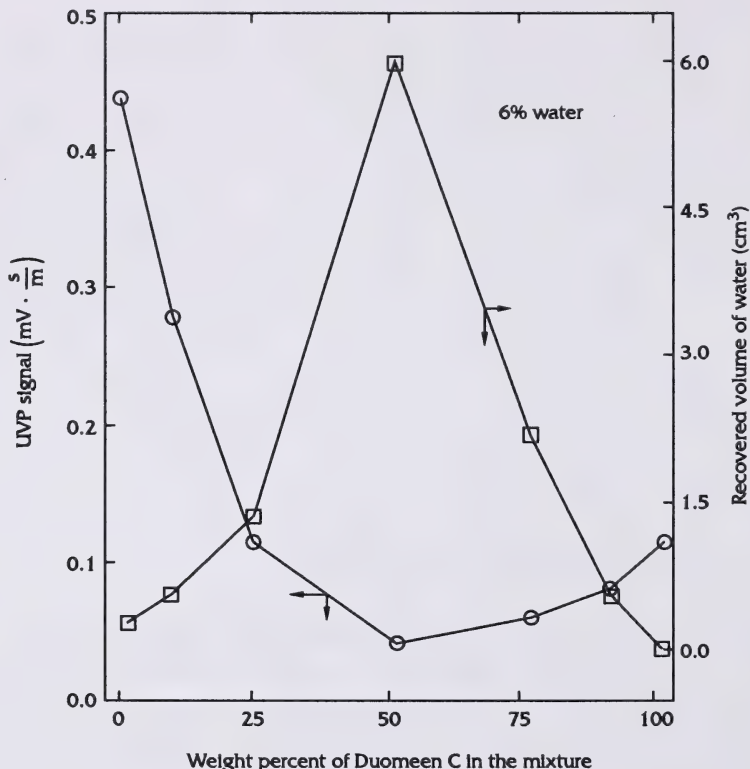
where  $\gamma_0$  and  $\gamma_t$  are the initial and equilibrium interfacial tensions, respectively, and  $t$  is the time to reach equilibrium interfacial tension. The spreading rate parameter was studied for a combination system consisting of an oil-soluble surfactant (Duomeen C) and a water-soluble surfactant (Aerosol OT). Measured spreading rates as a function of percent Duomeen C are shown in Figure 4.22. In Figure 4.23 the UVP, as measured by electrokinetic sonic analysis (see methods for investigating interfacial charge, this chapter), and water released by centrifugation are shown for the same surfactant system. The correspondence between Figure 4.22 and 4.23 is apparent. This study showed the potential for evaluating coagulation in water-in-oil emulsions using electroacoustic techniques. In a later work, Chow et al., (1991) applied the electroacoustical technique to monitor the chemical induced flocculation of water droplets in naphtha diluted froth.



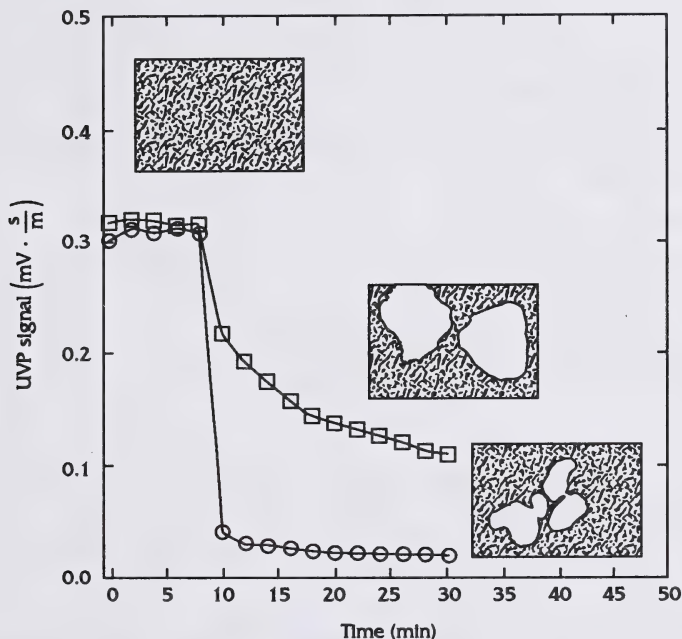
**Figure 4.22.** The measured spreading rate parameter (Eqn 4.16) as a function of the weight percent Duomeen C in the mixture of Duomeen C and Aerosol OT. Total surfactant concentration was 100 ppm. From Isaacs et al. (1990).

### Sedimentation rates of solids in organic media: Tyerman (1989)

investigated the sedimentation of kaolinite in organic solvents and in solutions of bitumen and various components of bitumen dissolved in organic solvents. The initial experiments examined the volume fraction of solids in the sediment (after 48 hours of sedimentation) as a function of initial asphaltene concentration for solutions of maltenes, asphaltenes, differing ratios of asphaltene/maltene, and bitumen in toluene. The results are shown in Figure 4.26. Initial asphaltene concentrations for the maltenes were calculated on the basis of 3.7 wt% asphaltenes in the maltenes. The volume fraction of solids in the sediment varied from 0.15 to about 0.40 as the initial asphaltenes concentration was increased. Figure 4.27 shows the same data plotted against the residual asphaltenes concentration in the solvent above the sediment, as determined by spectrophotometry. The absence of asphaltenes in the solvent above the sediment indicated that the asphaltenes had been adsorbed onto the solids. For the samples with asphaltenes alone, the adsorption was almost complete, suggesting that



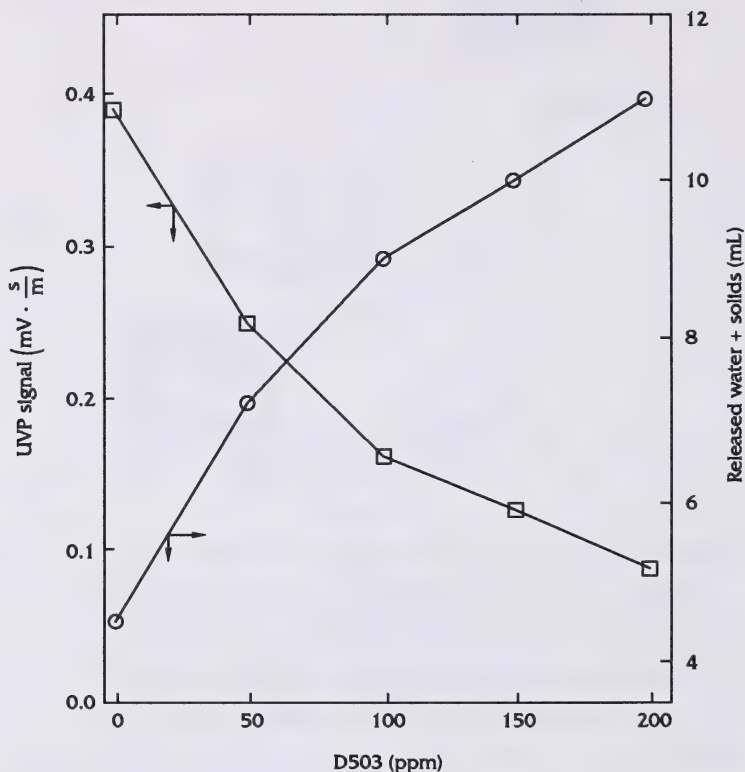
**Figure 4.23.** Comparison of the Ultrasound Vibration Potential (UVP) with the volume of recovered water in the centrifuge for a 6 vol% water-in-Leduc crude emulsion. Shown here as a function of the percent of Duomeen C in a demulsifier combination. Demulsifier combination was a Duomeen C and Aerosol OT mixture at a total concentration of 100 ppm. UVP signal acquired 20 minutes after addition of demulsifier. From Isaacs et al. (1990).



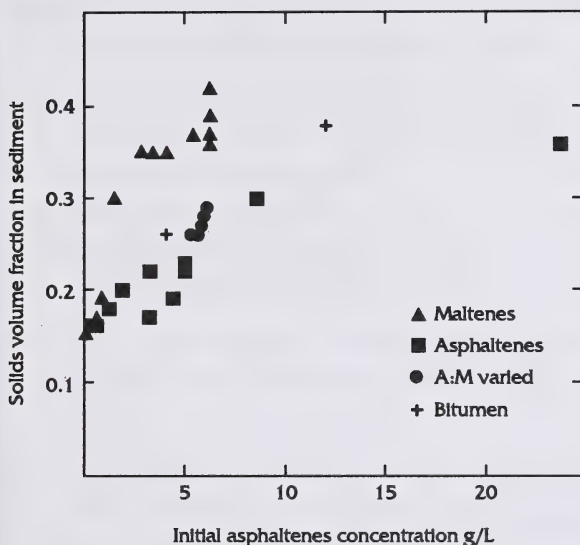
**Figure 4.24.** The sensitivity of the Ultrasound Vibration Potential (UVP) signal to changes in water droplet size in the naphtha-diluted froth. Demulsifiers were added at 8.0 minutes after the start of the experiment. Samples were withdrawn and microphotographs were taken at 6.0 and 28.0 minutes after the start of the experiment. From Chow et al. (1990).

the compaction of the sediment was caused by adsorbed asphaltenes, rather than dissolved asphaltenes. The situation with maltenes in the presence of asphaltenes is more complex. Maltenes decreased the effect of low concentrations of asphaltenes. This suggested a competitive adsorption resulting in displacement of asphaltenes from the solid surface by the maltenes (see below). However, with high concentrations of both asphaltenes and maltenes in solution, the sediment was denser than with asphaltenes alone. Figure 4.28 is analogous to Figure 4.27, but with naphtha rather than toluene.

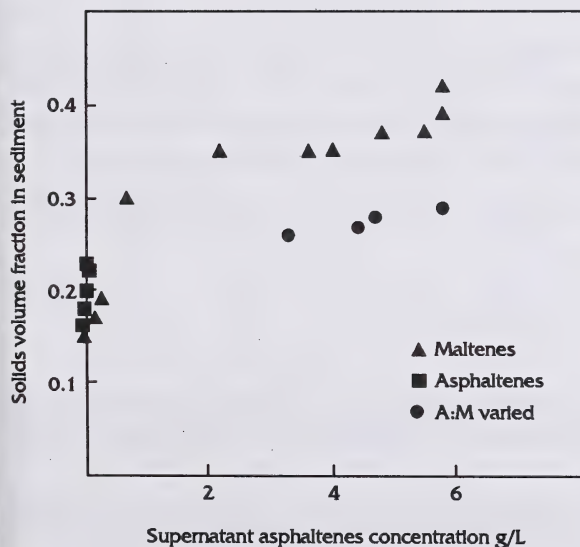




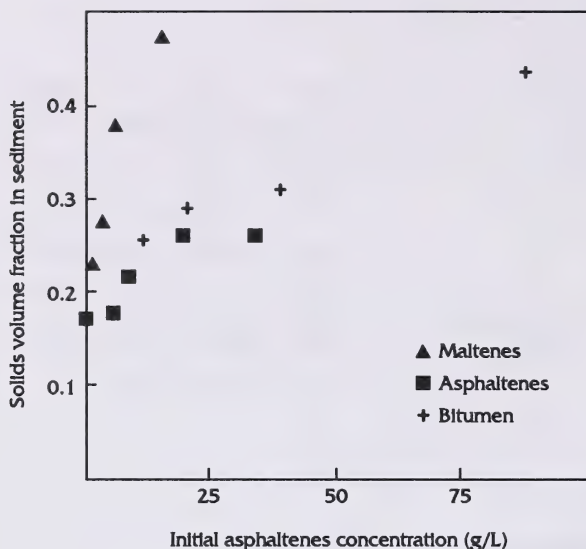
**Figure 4.25.** Comparison of the Ultrasound Vibration Potential (UVP) signal with the released volume of water plus solids after centrifugation as a function of demulsifier concentration for the naphtha diluted froth. From Chow et al. (1990).



**Figure 4.26.** The volume fraction of kaolinite in the sediment as a function of initial asphaltene concentration. Shown here for a continuous phase of maltenes, asphaltenes, different ratios of asphaltene/maltenes, and bitumen dissolved in toluene. From Tyerman (1989).



**Figure 4.27.** The same as Figure 4.26 but shown as a function of the supernatant asphaltene concentration. The figure illustrates that the adsorption of asphaltene onto the kaolinite is somewhat hindered by the presence of the maltene fraction. From Tyerman (1989).



**Figure 4.28.** The same as Figure 4.26 but the listed components dissolved in naphtha. From Tyerman (1989).

Adsorption of asphaltenes from toluene or naphtha onto kaolinite or solids recovered from froth was studied by spectrophotometry of the supernatants. Results were fitted using a Langmuir isotherm model (Tyerman, 1989). With bitumen solutions, there was no appreciable adsorption of the maltenes. The experiments were extended, using separated maltenes and asphaltenes. With the higher ratio of maltenes to asphaltenes there was evidence for competitive adsorption of the maltenes and asphaltenes (Tyerman, 1992). Other authors (Wasan and Menon, 1987) have reported that maltenes components may also adsorb on clays, so this result is not surprising. The adsorption clearly affects the interfacial properties, as demonstrated in settling experiments.

## REFERENCES

- Babchin, A.J., Chow, R.S., and Sawatzky, R.P. Electrokinetic measurements by electroacoustical methods, *Advances in Colloid and Interface Science* (1989) 30, 111–151.
- Bowman, C.W. Mining the Athabasca tar sands, *Science Journal* (1969, November) 5A, #5, 28–33.

- Bowman, C.W. Molecular and interfacial properties of Athabasca tar sands, Proceedings, 7th World Petroleum Congress (1967) 3, 583–603.
- Boyce, J.F., Schurcky, F., Rotenberg, Y., and Neumann, A.W. The measurement of surface and interfacial tension by the axisymmetric drop technique, *Colloids and Surfaces* (1984) 9, 307–317.
- Chow, R.S., and Takamura, K. Electrophoretic mobilities of bitumen and conventional crude-in-water emulsions using the laser Doppler apparatus in the presence of multivalent cations, *J. Coll. Interface Sci.* (1988) 125, 212–225.
- Chow, R.S., and Burgess, N. Electrokinetic properties of tailings from hot water processing of Athabasca oil sands, Alberta Research Council technical report, 1989.
- Chow, R.S., Huang, H., and Isaacs, E.E. The dewatering of naphtha diluted froth, Alberta Research Council internal report, 1991.
- Chow, R.S. The stability of kaolinite-in-water dispersions, *Colloids and Surfaces* (1991) 61, 241–253.
- Danielson, L. Syncrude internal report, 1990.
- Dobrogowska, C., and Hepler, L.G. unpublished.
- Healy, T.W., and White, L.R. Ionizable surface group models of aqueous interfaces, *Advances in Colloid and Interface Science* (1978) 9, 303–345.
- Heimenz, P. *Principles of colloid and surface chemistry*, (1977), Marcel Dekker, New York, pp 226–228.
- Hepler, L.G., and Hsi, C., ed. *AOSTRA technical handbook on oil sands, bitumens and heavy oils*, (1989), Alberta Oil Sands Technology and Research Authority, Edmonton.
- Hunter, R.J. *Zeta potential in colloid science*, (1981), Academic Press, New York, pp 248–252.
- Isaacs, E.E., and Morrison, D.N. Interfacial films at the Athabasca bitumen/water interface, *AOSTRA J. Research* (1985) 2, 113–119.



- Isaacs, E.E., Huang, H., Babchin, A.J., and Chow, R.S. Electroacoustical method for monitoring the coalescence of water-in-oil emulsions, *Colloids and Surfaces* (1990) 46, 177–192.
- Jennings, J.W., and Pallas, N.R. Effective method for determination of interfacial tensions from drop profiles, *Langmuir* (1988) 4, 959–967.
- Kasperski, K.L., Hepler, C.T., and Hepler, L.G. Viscosities of dilute aqueous suspensions of montmorillonite and kaolinite clays, *Can. J. Chem.* (1986) 64, 1919–1924.
- Leja, J., and Bowman, C.W. Application of thermodynamics to the Athabasca tar sands, *Can. J. Chem. Eng.* (1968) 46, 479–481.
- Levine, S., and Sanford, E. Stabilization of emulsion drops by fine powders, *Can. J. Chem. Eng.* (1985) 63, 258–268.
- O'Brien, R.W., and White, L.R. Electrophoretic mobility of a spherical colloidal particle, *J. Chem. Soc., Faraday Trans. 2*, (1978) 73, 1607–1678.
- Okada, K., Akagi, Y., Kogure, M., and Yoshioka, N. Effect of surface charges of bubbles and fine particles on air flotation process, *Can. J. Chem. Eng.* (1990) 68, 393–399.
- Rand, B., and Mellon, I.E. Particle interactions in aqueous kaolinite suspensions, I. Effect of pH and electrolyte upon the mode of particle interaction in homoionic sodium kaolinite suspensions, *J. Coll. Interface Sci.* (1977) 60, 308–320.
- Sawatzky, R.P., and Babchin, A.J., Hydrodynamics of electrophoretic motion in an alternating electric field, *J. Fluid Mechanics* (1992) in press.
- Schramm, L.L., Smith, R.G., and Stone, J.A. A surface-tension method for the determination of anionic surfactants in hot water processing of Athabasca oil sands, *Colloids and Surfaces* (1984) 11, 247–263.
- Schramm, L.L., and Smith, R.G. The influence of natural surfactants on interfacial charges in the hot-water process for recovering bitumen from the Athabasca oil sands, *Colloids and Surfaces* (1985) 14, 67–85.

- Schramm, L.L., and Kwak, J.C.T. The rheological properties of an Athabasca bitumen and some bituminous mixtures and dispersions, *J. Can. Pet. Tech.* (1988, January–February) 27, 26–35.
- Schramm, L.L. The influence of suspension viscosity on bitumen rise velocity and potential recovery in the hot water flotation process for oil sands, *J. Can. Pet. Tech.* (1989, May–June) 28, 73–80.
- Schramm, L.L. Petroleum emulsions, chapter 1 in *Emulsions: fundamentals and applications in the petroleum industry*, (1992) ed. L.L. Schramm, Advances in Chemistry Series 231, American Chemical Society, Washington.
- Schramm, L.L., and Hepler, L.G. Surface and interfacial tensions of aqueous dispersions of charged colloidal particles (clays), Submitted for publication.
- Seyer, F.A., and Gyte, G.W. Viscosity, Chapter 4 in *AOSTRA technical handbook on oil sands, bitumens and heavy oils*, (1989) ed. L.G. Hepler and C. Hsi, Alberta Oil Sands Technology and Research Authority, Edmonton.
- Shaw, D.J. Introduction to colloid and surface chemistry, (1980), Butterworths, London, pp150–155.
- Shu, W.R. A viscosity correlation for mixtures of heavy oil, bitumen, and petroleum fractions, *Soc. Pet. Eng. J.* (1984) 24, 277–282.
- Srinivasan, N.S., Spitzer, J.J., and Hepler, L.G. Electrophoretic properties of oil sands tailings and constituent clays in aqueous suspensions, *J. Can. Pet. Tech.* (1982, July–August), 21, 25–30.
- Swanson, V.F. The development of formulae for direct determination of free settling velocity for any size particle, *Soc. Min. Eng. Trans. AIME* (1967) 238, 160–166 and (1975) 258, 102–103.
- Takamura, K., and Chow, R.S. A mechanism for initiation of bitumen displacement from oil sand, *J. Can. Pet. Tech.* (1983, November–December) 22, 1–9.
- Takamura, K., and Chow, R.S. The electric properties of the bitumen/water interface Part II, application of the ionizable surface-group model, *Colloids and Surfaces* (1985) 15, 35–48.

- Takamura, K., and Wallace, D. The physical chemistry of the hot water process, J. Can. Pet. Tech. (1988, November–December) 27, 98–106.
- Takamura, K., and Isaacs, E.E., Interfacial properties, Chapter 5 in *AOSTRA technical handbook on oil sands, bitumens and heavy oils*, (1989) ed. L.G. Hepler and C. Hsi., Alberta Oil Sands Technology and Research Authority, Edmonton.
- Tyerman, W.J.R. Function of natural and model surfactants, Syncrude internal report, 1989.
- Tyerman, W.J.R. Sedimentation of kaolinite in toluene or naphtha, Syncrude internal report, 1989.
- Tyerman, W.J.R. Interaction of surfactants with dispersions of bitumen-solvent-solids-water, AOSTRA J. Research (1989) 5, 183–193.
- Tyerman, W.J.R. Nature of the asphaltenes/maltenes system, Syncrude internal report, 1990.
- Tyerman, W.J.R., and Smith, R.G. Electrophoretic mobilities, correlation of extraction data, Syncrude internal report, 1990.
- Tyerman, W.J.R., personal communication, 1992.
- Usui, S., and Sasaki, H. Zeta potential measurements of bubbles in aqueous surfactant solutions, J. Coll. Interface Sci. (1978) 65, 36–45.
- Verwey, E.J.W., and Overbeek, J.Th.G. *Theory of the stability of lyophobic colloids*, (1948), Elsevier, New York.
- Wasan, D.T., and Menon, V.B. Adsorption of maltenes on sodium montmorillonite, Colloids and Surfaces (1987) 25, 387–400.

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## *A Role for Surfactants in the Hot Water Process*





## INTRODUCTION

There has been speculation beginning even in the pioneering work of Karl Clark (1944) that water soluble surfactants are produced when oil sand is treated with sodium hydroxide in the hot water process and that these surfactants play a role in the process. A first attempt to isolate the surfactant products was made by Bowman (1967) who foam fractionated water from the hot water process to produce a surface active concentrate. He constructed a surface tension/concentration curve for the surfactant isolated in this fashion and identified the surfactant as a carboxylate by infrared analysis. The infrared spectrum of the concentrate, which was isolated from alkaline solution, had a carboxylate peak at  $6.4\text{ }\mu\text{m}$ , which shifted at low pH to a carboxylic acid peak at  $5.8\text{ }\mu\text{m}$ . Bowman went on to speculate that the carboxylate surfactant was beneficial to the hot water process because it acted to lower interfacial tension between the various phases present in the system. Somewhat later Bowman and Baptista (1969) concluded from a detailed consideration of the infrared spectrum of the surfactant that the compound was a sodium naphthenate.

Naphthenic acids are known to exist in the so-called acidic crudes and samples have been isolated recently and characterized by mass spectrometry (Dzidic et al., 1988; Fan, 1991). The material as isolated from acidic crude oil is a complex mixture of paraffinic and mono-, di-, tri-, and higher polycyclic acids. Presumably the naphthenates in process water from hot water extraction of bitumen are similar but to date these naphthenates have not been characterized.

The water soluble organic materials were also studied by Moschopedis, Fryer, and Speight (1977), who isolated the water soluble organics from tailings pond water by the steps of acidification, settling (to allow the clays to settle) and extraction with methylethylketone. The methylethylketone was removed by evaporation to leave a residue of organic material. Infrared analysis of this product indicated that it contained a carboxylic acid (peak at  $1700\text{ cm}^{-1}$ ) and oxygenated sulfur compounds (peaks at  $1030\text{ cm}^{-1}$  and  $1080\text{ cm}^{-1}$ ). The organic material was also dissolved in quinoline and a potentiometric titration was done using ammonium hydroxide in isopropanol. The titration results indicated the presence of three acids with half-neutralization potentials that suggested the acids were a sulfonic acid type, a carboxylic acid type, and a phenolic type. In a separate publication (Speight and Moschopedis, 1977/1978) it was shown that the organic acids as isolated by this

procedure acted in 0.1 N sodium hydroxide to lower surface tension and interfacial tension (as measured against n-decane).

The surface active agents in the aqueous phase from the hot water flotation process were also studied by Ali (1978). Surface active material was isolated from tailings water from the hot water process by foam fractionation followed by azeotropic removal of the water from the concentrate with toluene. The toluene was then concentrated to a small volume and a toluene insoluble fraction was collected by filtration. Water was added to the solids, followed by hydrochloric acid, and the mixture was extracted with ether. The isolate was examined by infrared analysis and exhibited absorptions characteristic of carboxylic acids and sulfonic acids. The presence of sulfonates in the toluene insoluble fraction was confirmed by treatment of the mixture of sodium salts with  $\text{PCl}_5$  which produced a product which had infrared bands characteristic of a sulfonyl chloride.

Burchfield and Hepler (1979) isolated organics from filtered pond water by acidification with hydrochloric acid to  $\text{pH} \approx 1.5$  followed by extraction with diethyl ether. The material isolated in this way had infrared bands at  $1703 \text{ cm}^{-1}$  (carbonyl) and  $1040 \text{ cm}^{-1}$  (sulfur-oxygen).

Proof that surfactants play a role in the hot water process was published in 1979 by Sanford and Seyer. In this study an average grade oil sand was processed using no sodium hydroxide (61% primary recovery) and using the optimum amount of sodium hydroxide (88% primary recovery). It was established for the experiment with sodium hydroxide by titration of the tailings with hydrochloric acid that the tailings did not contain any excess sodium hydroxide. Instead an end point at  $\text{pH} \approx 4.5$  was present, which was ascribed to sodium carboxylates similar to sodium oleate. The tailings from the experiment using sodium hydroxide were centrifuged to remove solids and concentrated by evaporation. The concentrate was added to the next experiment so that any water soluble surface active agents produced in the sodium hydroxide experiment were recycled. The experiment was carried out without sodium hydroxide. A good primary recovery (87%) was obtained, providing evidence that surfactants are responsible for the recovery improvement obtained with sodium hydroxide. Sanford and Seyer were also able to show that an improvement in primary recovery over the no-additive case could be obtained using commercial surfactants. The surfactants that were tested included Tide, sodium oleate, and sodium lignosulfonate.

Carboxylic acids have also been isolated by Misra, Aguilar, and Miller (1981) from process water produced by hot water processing of Utah tar sands. The isolation procedure involved filtration of the process water, concentration of the filtrate to a small volume, acidification with hydrochloric acid, and extraction with carbon tetrachloride. The infrared spectrum of the isolated material had a peak at  $1708\text{ cm}^{-1}$  indicating a carboxylic acid. Potentiometric titration of the acidic isolate indicated an acid dissociation constant of  $\text{pK}_a \approx 5$

## **A METHOD FOR MEASUREMENT OF SURFACTANT CONCENTRATIONS**

An analytical method for determination of concentrations of surface active species in tailings water from the hot water process was published in 1984 (Schramm, Smith, and Stone (1984a). In this method ultrafiltered process water is titrated with a standard solution of cetyltrimethylammonium bromide (CETAB) and the progress of the titration is monitored by following the surface tension of the solution. As the titration progresses, surface tension decreases rapidly until all the anionic surfactant is consumed and then continues to decrease but at a slower rate as excess CETAB builds up in the titrated solution. In theory it should be possible to detect the end point as the point at which the very fast rate of decrease changes to a very slow rate of decrease. In practice this method performs poorly and it is better to determine concentrations of unknown solutions by matching the unknown titration curves to titration curves for known concentrations of standard purified surfactants.

The fast decrease in surface tension observed in the CETAB titrations is believed to be due to the formation of a highly surface active complex between the anionic surfactants in the process water and the cationic surfactant (CETAB) used for the titration.

The CETAB titration procedure is effective for both sulfonate surfactants and carboxylate surfactants, so titrations on tailings water as produced from the hot water process give the total concentration of all anionic surfactants. The concentration of sulfonate surfactants can be obtained by adjusting the pH of the process water to 3.0, which serves to convert the carboxylate surfactants to carboxylic acids which do not form a complex with CETAB. The sulfonate surfactants remain as sulfonates at this



pH since acidities corresponding to  $\text{pH} < 3$  are required to convert sulfonates to sulfonic acids. Consequently it is possible to determine the concentration of sulfonate surfactants by a CETAB titration at  $\text{pH} \approx 3.0$  and the concentration of total anionic surfactants by a titration on the slightly alkaline process water as received. The difference should equal the concentration of carboxylate surfactants.

Experiments with pure surfactant compounds (sodium laurate and sodium n-octyl sulfonate) revealed that the actual shapes of the surface tension plots (surface tension vs amount of CETAB added) were slightly dependent on the salt concentration of the solution. For the procedure involving comparison of the unknown curve with curves of known concentrations of standards to work properly, it is necessary to prepare the standards with the same salt concentration as the unknown. In practice this is done by measuring the concentration of carbonate and bicarbonate by acid titration and the concentration of sulfate and chloride by ion chromatography. The standards are then prepared by making an aqueous solution of the standard with the appropriate quantities of sodium carbonate, bicarbonate, chloride, and sulfate. Initially the standards used were sodium laurate at the as-received pH and sodium n-octyl sulfonate at  $\text{pH} \approx 3.0$ . Later, sodium naphthenate was used at the as-received pH.

## **PRIMARY RECOVERY AND CARBOXYLATE SURFACTANTS**

To elucidate the role played by surfactants in the hot water process, several oil sands of various grades were processed in the Syncrude batch extractor, each at several concentrations of sodium hydroxide (Schramm, Smith, and Stone, 1984b). Primary recoveries and surfactant concentrations in the process water were determined. The oil sands behaved in the normal manner, giving primary recoveries which were low when no sodium hydroxide was used and which increased to a maximum value as the amount of sodium hydroxide was increased, and then declined to lower values as the amount of sodium hydroxide was further increased. Rich grade oil sands gave maximum primary recovery when no sodium hydroxide was used while average grade oil sands required about 0.02 to 0.04 wt% sodium hydroxide to yield maximum primary recovery. Low grade oil sands required even higher concentrations of sodium hydroxide for maximum primary recovery, which in some cases was as much as 0.20 wt% sodium hydroxide. Previous work (Sanford, 1983)

has indicated that there is a strong correlation between the amount of sodium hydroxide needed for maximum primary recovery and the fines ( $<44\ \mu\text{m}$ ) content of oil sands.

The surfactant concentrations in process water were found to increase in all cases with increasing amount of added sodium hydroxide. Carboxylate surfactant concentrations were in most cases in the range from 0 to 0.20 meq/L with the low concentrations occurring at low concentrations of sodium hydroxide. Sulfonate surfactant concentrations were in most cases quite low, ranging from 0.02 to 0.07 meq/L but for some oil sands higher concentrations were found. Carboxylate surfactant concentrations gave linear plots when plotted vs the amount of sodium hydroxide added. Experiments with no added sodium hydroxide gave carboxylate surfactant concentrations near 0.12 meq/L for rich oil sands, 0.04 to 0.08 meq/L for average grade oil sands and near zero for low grade oil sands. The carboxylate surfactants must therefore exist as such in the oil sand or be formable from oil sand components and the natural basic materials that exist in oil sands. The added sodium hydroxide acts to produce an increase in the concentration of carboxylate surfactants.

Primary recoveries for each of the oil sands in the study were plotted as a function of carboxylate surfactant concentration and it was immediately apparent that maximum primary recovery for all the oil sands (rich, average, and low grade) occurred at the same concentration of carboxylate surfactant. This finding was very much in contrast to the finding that the amount of sodium hydroxide needed for maximum primary recovery varies greatly with oil sand grade. The concentration of carboxylate surfactant needed for maximum primary recovery was about 0.12 meq/L and this concentration has been labelled the critical concentration. In practice, rich oil sands have the critical concentration of carboxylate surfactant in the process water when no sodium hydroxide is added while average grade oil sands require 0.02 to 0.04 wt% sodium hydroxide to produce the critical concentration and low grade oil sands can require from 0.04 to as much as 0.20 wt% sodium hydroxide.

The finding that oil sands gave maximum primary recovery at the same carboxylate surfactant concentration was seemingly independent of the sulfonate surfactant concentration. To date a wide variety of oil sands have been examined and it has been found that they all give maximum primary recovery at the critical concentration of carboxylate surfactant. The relationship between maximum primary

recovery and carboxylate surfactant concentration held true in spite of a large variation in sulfonate surfactant concentration, which ranged from 0.00 to 0.20 meq/L at the same time that carboxylate surfactant concentration was 0.12 meq/L.

The critical concentration of 0.12 meq/L cited above is thought to apply only to process water from the Syncrude batch extractor as operated according to the standard procedure given in Chapter 2 and Appendix 3. This process uses 1050 mL of water for 500 g of oil sand or about 2 parts of water for 1 part of oil sand. In contrast, the Syncrude pilot plant and the commercial equipment use a total of 0.7 parts of water to 1 part oil sand. Consequently the concentrations of carboxylate surfactant in process water in the two cases would be expected to differ. Evidence exists (Schramm and Smith, 1989) that the carboxylate surfactants act at the slurry stage of the process and it is the concentration at this stage that is especially important. Since the Syncrude batch extractor uses 150 mL of water at the slurry stage, a simple back calculation (ignoring any contribution due to water in the oil sand) indicates that the tailings stage critical concentration becomes 0.84 meq/L at the slurry stage and it may be that this critical concentration is the one that is common to all the processes. The total amount of surfactant produced from a given quantity of oil sand at the condition of optimum recovery can also be calculated and would be expected to be the same for all the processes.

## **SURFACTANTS AND THE MECHANISM OF THE PROCESS**

The hot water process involves two process steps. The first of these requires displacement of the bitumen from the solids, while the second step involves aeration of the bitumen droplets so that the bitumen will float. It is known (Takamura, 1982) that oil sand solids are predominately water wet with the bitumen and solids separated by a water film of about 10 nm thickness. It is thought that this water film makes for easy separation of bitumen from the solids because this step simply involves increasing a separation that already exists. It is also known that the density of bitumen is very close to that of water and it is apparent that aeration is a necessary step for bitumen flotation to occur.

For the processes described above to take place efficiently many interfacial transformations need to take place. A thermodynamic analysis (Leja and Bowman,

1969) established some fundamental understanding of the interfacial changes that are needed for successful operation of the process. From a thermodynamic point of view, a spontaneous change in state, such as displacement of oil from solids or attachment of oil to air, will take place if there is a corresponding decrease in the free energy of the system. The governing thermodynamic expression was taken as the Helmholtz free energy relationship, which for conditions of constant volume and temperature states that the change in the free energy of a system is equal to the sum of chemical, electrical, and surface work. The Helmholtz relationship is presented below as equation 5.1:

$$(5.1) \quad dF = \sum \mu dn + \sum \phi dq + \sum \gamma dA$$

In the above equation  $\mu$  is chemical potential,  $n$  is chemical quantity,  $\phi$  is the potential across the interface,  $q$  is the electrical charge at the interface,  $\gamma$  is interfacial tension, and  $A$  is interfacial area.

Leja and Bowman discussed the common practice of considering only the surface work term and even then of making the further assumption that the area term can be neglected. They pointed out that the simplification of neglecting the area term cannot be used when considering displacement of oil from solids because the process of displacement of oil from around the surface of a solid to form a discrete droplet must result in a large decrease in the oil/water interfacial area. They concluded that the large changes in interfacial areas should drive the displacement of oil from solids. The same considerations apply to the attachment of oil to air, although in this case the authors were able to conclude that filming of bitumen on air bubbles would be favored over an attachment process.

Leja and Bowman also pointed out that the electrical work term cannot be neglected for the oil sand system. They suggested that one of the expected functions of surfactants in the hot water process would be to place negative charges on the solid particles, the bitumen droplets, and the air bubbles. Calculations of the electrical work term, based on literature data, indicated that this term could easily equal the surface work term.



## **PARTICLE CHARGES AND CARBOXYLATE SURFACTANTS**

In light of the thermodynamic considerations described above, it appears likely that the hot water process proceeds largely because of the changes that occur in interfacial tensions and in surface charges brought about by the carboxylate surfactants that are generated in the process when sodium hydroxide reacts with acidic materials in the bitumen. The electrophoretic mobilities of tailings fine solids from the hot water process have been reported as a function of pH (Srinivasan, Spitzer, and Hepler, 1982). These authors found that the electrophoretic mobilities of the solids were negative at the natural pH (8 to 9) but became less so as the solution pH was reduced. The reduced electrophoretic mobility can be explained as caused by a reduction in carboxylate surfactant concentration due to conversion of carboxylate to carboxylic acid.

Electrophoretic mobilities for oil sand fine solids and bitumen droplets in water from the process have been measured (Schramm and Smith, 1985) as functions of carboxylate surfactant concentrations and the results appear to confirm that charges of particles are important in the hot water process.

The electrophoretic mobilities, mentioned above, were measured using a Rank Brothers' microelectrophoresis apparatus (Mark II) fitted with a rotating prism and a video-viewing system. Suspensions of fine solids were prepared by adding a drop of secondary tailings to about 50 ml of ultrafiltered secondary tailings. The result was a 1% dispersion of oil sand fine solids in the original process solution (preserving both the original electrolytes and surfactants). Emulsions of bitumen were prepared by adding a drop of froth from the batch extractor experiment to about 50 ml of ultrafiltered secondary tailings from the same experiment and dispersing the bitumen with an ultrasound generator. The result again was a 1% dispersion of bitumen droplets in the original process solution.

Electrophoretic mobilities of fine solids and bitumen droplets were measured for rich, average, and low grade oil sands over a range of sodium hydroxide concentrations. The carboxylate surfactant concentrations were also measured in process water from each of the experiments. In all cases (rich, average, and low grade) the electrophoretic mobilities of the solids became more negative as the carboxylate surfactant concentration increased, but reached a plateau at or near the critical surfactant concentration and remained at this plateau value even at surfactant

concentrations above the critical concentration. The electrophoretic mobilities of the bitumen droplets also became more negative as the carboxylate surfactant concentration increased but reached a maximum (negative) and then fell slightly to lower absolute values at surfactant concentrations above the critical concentration.

The trends of the fine particle and bitumen droplet electrophoretic mobilities agree with the suggestion made by Leja and Bowman (1969) that one of the roles of surfactants in the hot water process is to place an electrical charge on the clay and bitumen particles and air bubbles. Maximum primary recovery in the process is now known to occur at a free carboxylate surfactant concentration of 0.12 meq/L and this maximum is also the point at which the total electrical charges on the fine solids and bitumen droplets are maximized. It seems probable that separation of bitumen from solids is facilitated by repulsion between the fine solids and the bitumen phases due to the high total electrical charge. As indicated by Leja and Bowman, changes in interfacial tension brought about by surfactants also provide a driving force for the separation.

Several experimental studies have established that gas bubbles are negatively charged in aqueous electrolyte solution, with the charge depending on pH and electrolyte concentration. Gas bubbles also have a negative charge in aqueous solutions of anionic surfactants. Studies of interest include Collins, Motarjemi, and Jameson, 1978; Fukui and Yuu, 1982; Kubota, Hayashi, and Inaoka, 1983; Yoon and Yordan, 1986; Okada and Akagi, 1987; Okada, Akagi, and Yoshioka, 1988; Laskowski, Yordan, and Yoon, 1989; Okada, Akagi, Kogure, and Yoshioka, 1990; Li and Somasundaran, 1991. Measurements have not yet been reported for bubbles in the hot water system but it appears probable that the bubbles are negatively charged because process water from the process contains both electrolytes and surfactants. If the bubbles do turn out to be negatively charged, then electrostatic repulsion between the bubbles and the negatively charged bitumen would be expected to act to prevent attachment. Offsetting this force, however, would be a driving force due to changes in interfacial tension and interfacial area as discussed by Leja and Bowman (1969). Further work is needed to identify and measure the forces involved.

The relationships noted between electrophoretic mobility and carboxylate surfactant concentration were, like the relationship between primary recovery and carboxylate surfactant concentration, independent of the concentration of sulfonate surfactant.

Electrophoretic mobilities for fine solids and bitumen droplets have been measured by Hupka and Miller (1991) for bitumen and for solids produced by hot water flotation of Utah tar sands. They also found that fine solids electrophoretic mobilities approached a negative plateau as surfactant concentration increased and that bitumen droplet electrophoretic mobilities tended to go through a negative maximum.

### **A Role for Sulfonate Surfactants**

Most oil sands, as described above, lead to plots of primary recovery vs amount of sodium hydroxide used which are smooth concave upward curves with a single maximum. Carboxylate surfactant concentrations in tailings water from processing these oil sands with sodium hydroxide have linear plots of carboxylate surfactant concentration vs sodium hydroxide.

However, oil sands that process abnormally do occur from time to time and, although they represent only a small fraction of the available oil sand, are of interest both from theoretical and practical points of view. One such oil sand has been described (Schramm and Smith, 1987a) and is of interest because it had two primary recovery peaks when primary recovery was plotted against amount of sodium hydroxide added.

The oil sand in question was processed both in the pilot plant and in the Syncrude batch extraction unit. In the pilot plant the first primary recovery peak occurred at about 0.02 wt% sodium hydroxide while the second peak occurred at about 0.05 wt% sodium hydroxide. Primary recoveries were about 85% for the first peak and about 80% for the second peak. Between the peaks at about 0.04 wt% sodium hydroxide the primary recovery was only about 20%. Similar peak behavior was observed in processing the oil sand in the batch extractor. Here the dip between the peaks was not as pronounced, with primary recovery down from the peak recovery to about 60%.

Surfactant concentrations were measured in process water from the batch extractor experiments and it was found that carboxylate surfactants did not appear in the process water at low sodium hydroxide concentrations. The first measurable amount of carboxylate surfactant was in the experiment at 0.04 wt% sodium

hydroxide. The concentration of carboxylate surfactant then increased as a linear function of sodium hydroxide and the critical concentration (0.12 meq/L) was reached at about 0.05 wt% sodium hydroxide. The data were interpreted as indicating that the second peak in the plot of primary recovery vs amount of sodium hydroxide added was due to the carboxylate surfactants, leaving open the question of responsibility for the first peak.

Sulfonate surfactant concentrations were also measured and these surfactants were found to be present in appreciable concentration in the experiment without added sodium hydroxide. Here the concentration was about 0.09 meq/L and this concentration increased linearly as the concentration of sodium hydroxide was increased. It was concluded that these surfactants were responsible for the first peak in the primary recovery curve. The peak occurred at a sulfonate surfactant concentration of 0.15 meq/L and this concentration has been referred to as the critical concentration for this surfactant.

Electrophoretic mobilities of bitumen droplets were also measured for each of the sodium hydroxide concentrations. Results of these measurements also showed two peaks when plotted vs amount of sodium hydroxide added. There was a first peak at about 0.02 wt% sodium hydroxide and a second peak at about 0.06 wt% sodium hydroxide. It appears that the peak at 0.02 wt% sodium hydroxide was due to the sulfonate surfactants while the peak at about 0.06 wt% sodium hydroxide was due to the carboxylate surfactants.

The work on normal oil sands served to establish that sulfonate surfactants do not interfere with enhancement of production by the carboxylate surfactants. If carboxylate surfactants are present they appear to be controlling and maximum primary recovery occurs at a concentration of 0.12 meq/L no matter what the concentration of sulfonate surfactant. Sulfonate surfactants only become controlling in the absence of carboxylate surfactants. Some evidence is quoted in the paper by Schramm and Smith (1987) to indicate that low concentrations of carboxylate surfactant do interfere with operation of the process by sulfonate surfactants. The interference takes the form of a reduction in primary recovery over what can be obtained when carboxylate surfactants are completely absent.



## SURFACTANTS AND OIL SAND AGING

It has been known for a long time that processibility curves (plots of primary recovery vs wt% sodium hydroxide added) change as oil sands sit in storage in the presence of air. The phenomenon has been termed aging and the aging process can cause an increase in the amount of sodium hydroxide needed to obtain maximum primary recovery and also a decrease in the maximum recovery. Not all oil sands age and for oil sands that do age the rate is faster if the oil sands are homogenized prior to storage. The work which established the information cited above is described in papers by Clark and Pasternack, 1949; Pasternack and Clark, 1951; Sanford and Seyer, 1979; and Sanford 1983.

Several mechanisms, which can be used to explain the changes that occur in processibility, are described in the literature. One of these proposes that it is dehydration of the oil sands as they sit in storage that causes the processibility changes. This theory is discussed in papers by Clark and Pasternack (1951) and by Ali (1975). The authors of these papers suggested that as the samples dry out in storage the bitumen becomes directly attached to the solids rather than separated by a thin layer of water and processibility deteriorates. This theory has been largely discounted today because it has proven possible (McConaghy, Paradowski, and Porteous, 1973) to get good primary recoveries using the standard process with no increase in sodium hydroxide from oil sands that have been completely dehydrated by exposure to the atmosphere.

Another mechanism is proposed in papers by Wallace and Henry (1984) and by Wallace, Henry, and Takamura (1989). This mechanism is based on the finding that the sulfate content of oil sands increases as oil sands age in the presence of air. Sulfate content was followed by extracting small samples of the oil sand with water and analyzing the water extract for sulfate. The authors propose that the sulfate is formed by oxidation of pyrite ( $\text{FeS}_2$ ) either by a chemical process or by a bacterial assisted chemical process. They explain the deterioration in froth quality and the loss of bitumen recovery as caused by coagulation of the fine particles during the process, which in turn is caused by the lower pH and the increased salt concentration.

Surfactant concentrations as produced from oil sands undergoing the aging process have been measured, with the results published by Schramm and Smith,

1987b. Two oil sands were studied, a low grade sample of marine origin containing about 8% bitumen and a rich oil sand of estuarine origin containing about 14% bitumen. Both oil sands were stored in polyethylene bags at 4°C in the presence of air. The low grade sample aged as described in the literature with the sodium hydroxide requirement for maximum primary recovery increasing with age and the maximum obtainable primary recovery decreasing as the sodium hydroxide requirement increased. Maximum primary recovery decreased from about 80% for the fresh oil sand to about 20% after 91 days of storage. Sodium hydroxide requirement increased from about 0.05 wt% to about 0.16 wt% over the same period of time.

Surfactant concentrations were measured in all cases and also plotted vs sodium hydroxide added. The straight line plots were shifted to the right with age with the result that the greater the age of the oil sand the greater the amount of sodium hydroxide needed to generate the critical concentration of carboxylate surfactant. In all cases the amount of sodium hydroxide needed to generate the critical concentration of surfactant was equal to the amount needed to reach maximum primary recovery. Sulfonate surfactant concentrations for this oil sand were high and in all cases above the 0.15 meq/L believed needed to operate the process. In most of the aged cases carboxylate surfactant was absent at low concentrations of sodium hydroxide. However, the expected recovery enhancement due to sulfonate surfactants did not occur, presumably because the concentration of this surfactant was in all cases above the critical concentration.

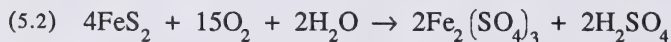
The results of work with this low grade oil sand established that the aging process interfered in some way with production of carboxylate surfactants. There was, however, at that time no indication of the nature of the interference.

The rich oil sand aged in a different fashion from the low grade oil sand. The plots of primary recovery vs sodium hydroxide added for aging of this oil sand showed progressive development of two peaks. There remained throughout a first peak of good primary recovery at near zero sodium hydroxide. If, as is usual, only low concentrations of sodium hydroxide had been investigated, the conclusion would have been that the oil sand did not age. It was only the use of higher than normal concentrations of sodium hydroxide that revealed that changes were taking place as the oil sand aged.

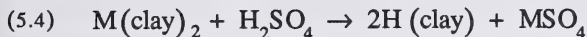
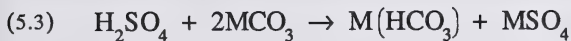
Plots of carboxylate surfactant concentration vs amount of sodium hydroxide added revealed that more and more sodium hydroxide was needed to produce the critical carboxylate surfactant concentration as the oil sand aged. At the same time, sulfonate surfactant concentration remained unchanged with a concentration of 0.15 meq/L occurring at near zero added sodium hydroxide. The authors interpreted the data as indicating that the recovery peak at zero sodium hydroxide was initially due to carboxylate surfactants because initially the concentration of carboxylate surfactants at zero sodium hydroxide was 0.12 meq/L. As the oil sand aged, the concentration of carboxylate surfactant at zero sodium hydroxide gradually reduced to zero and yet the primary recovery peak at zero sodium hydroxide did not change. The authors argued that the peak was now no longer due to carboxylate surfactants, but instead due to the sulfonate surfactants with 0.15 meq/L believed to be the critical concentration for these surfactants. The second peak which developed as the oil sand aged, was explained as due to the carboxylate surfactants.

The net result of the work on this rich oil sand was the conclusion that this oil sand, even though it continued to give good primary recovery at zero added sodium hydroxide, was in fact aging. The aging process takes the same form as the aging process for low grade oil sands. In both cases aging interferes with the production of carboxylate surfactants and an increase in the amount of added sodium hydroxide is needed to generate the critical concentration of carboxylate surfactant.

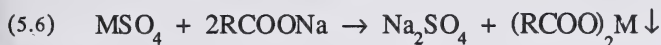
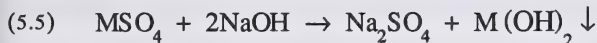
A mechanism has been proposed (Schramm and Smith, 1987c) which explains the difficulty in producing carboxylate surfactant from aged oil sands. According to this mechanism, the aging process involves as a first step the oxidation of pyrite ( $\text{FeS}_2$ ) to ferric sulfate and sulfuric acid. This reaction can be either a direct chemical oxidation or a bacterially assisted chemical oxidation and the overall reaction can be represented as follows:



The sulfuric acid produced in the above described reaction would be expected to react with basic materials contained in oil sand such as divalent carbonates and divalent clays. The reactions involved can be written as given below:



The net effect of the series of reactions is to produce cations such as ferric, calcium, and magnesium. It is proposed that the cations go on to react either with sodium hydroxide or with sodium carboxylates to form either insoluble hydroxides or insoluble carboxylates. In either event there would be an increase in the sodium hydroxide requirement for the production of the critical carboxylate surfactant concentration and thence maximum primary recovery. The reactions involved in this last step of the aging process can be written as follows:



The proposed mechanism explains the need for ever-increasing amounts of sodium hydroxide as oil sands age and a possible explanation follows for the reduction in maximum obtainable primary recovery that also occurs. The authors proposed that the reduced recovery is the result of the increased salt concentration (i.e., increased sodium bicarbonate) that occurs as the sodium hydroxide concentration is increased. They have been able to demonstrate a similar effect on recovery when a salt such as sodium chloride is added to oil sands. Here, even though the concentration of carboxylate surfactant remains at the critical concentration, there is a reduction in primary recovery due to the added salt.

As a test of the proposed theory, Schramm and Smith (1987c) processed an aged oil sand with added ethylenediamine tetraacetic acid. If the proposed series of aging reactions is correct, the use of EDTA should complex the polyvalent cations and reverse the effects of aging. An oil sand containing 10.6% bitumen was used in the study. The fresh oil sand required about 0.03 wt% sodium hydroxide for



maximum primary recovery, which became about 0.08 wt% after 125 days of aging. When EDTA was added to batch extractions on the aged oil sand the sodium hydroxide requirement for maximum primary recovery returned to about 0.03 wt%. The EDTA did not restore primary recovery for the aged oil sand to the non-aged value. Carboxylate surfactant concentrations were also found to return to normal when EDTA was used. The produced water was analyzed for metal cations for the optimum sodium hydroxide concentration for the aged oil sand with and without EDTA. For the case without EDTA the process water was found to contain mainly sodium with only a trace of calcium. The process water does not contain appreciable quantities of divalent ions because, in the standard process, they are precipitated as divalent carbonates and clays. For the case using EDTA the produced water was found to contain iron, calcium, manganese, and magnesium, with calcium being predominant. The total moles of dissolved metallic species was about equal to the total moles of added EDTA. It is evident that EDTA has acted to bind the divalent cations and prevent their precipitation. The experimental results are in agreement with the proposed mechanism.

The Schramm and Smith mechanism, like the Wallace, Henry, and Takamura mechanism, predicts that the aging process will generate sulfate. Schramm and Smith (1987) were also able to show that sulfate is produced when oil sands age and demonstrated that data on sulfate produced as a function of time could be used to calculate aging rates for oil sands. Both groups recommended low temperature storage as a practical way to prevent aging of oil sands to be used for laboratory investigations.

## **CONCLUSIONS**

The evidence, summarized above, for involvement of surfactants in the hot water process is compelling. The surfactant theory, as demonstrated in the preceding discussion, can be used to explain much of the knowledge that has accumulated over the years about the hot water process. In particular, the theory has been used to explain the variability in the amount of sodium hydroxide needed for maximum primary recovery with oil sand grade, to explain the existence of oil sands with two primary recovery peaks, and to explain the aging phenomena that occurs in oil sands during storage. The theory has also been used to explain the role of slurry water quantity in the process and to provide an understanding of temperature effects

(Schramm and Smith, 1989). It has also been used to rationalize mixing effects (Schramm, Smith and Stone, 1985) and to explain the effect of overburden contamination on oil sand processibility (Smith and Schramm, 1989).

## **REFERENCES**

- Ali, L.H. Studies on the ageing phenomenon of tar sand, *Fuel* (1975) 54, 223.
- Ali, L.H. Surface-active agents in the aqueous phase of the hot-water flotation process for oil sands, *Fuel* (1978) 57, 357–360.
- Baptista, M.V. and Bowman, C.W. The flotation mechanism of solids from the Athabasca oil sands, Preprint, 19th Can. Chem. Eng. Conf., Edmonton, Alberta (1969).
- Bowman, C.W. Molecular and interfacial properties of Athabasca tar sands, *Proceedings, Seventh world petroleum congress* (1967) 3, 583–603.
- Burchfield, T.E., and Hepler, L.G. Some chemical and physical properties of tailings water from oil sand extraction plants, *Fuel* (1979) 58, 745–747.
- Clark, K.A., and Pasternack, D.S. The role of very fine mineral matter in the hot water separation process as applied to Athabasca bituminous sand, *Research Council of Alberta* (1949), Report No. 53.
- Collins, G.L., Motarjemi, M., and Jameson, G.J. A method for measuring the charge on small gas bubbles, *J. Colloid and Interface Sci.* (1978) 63, 69–75.
- Dzidic, I., Sommerville, A.C., Raia, J.C., and Hart, H.V. Determination of naphthenic acids in California crudes and refinery wastewaters by fluoride ion chemical ionization mass spectroscopy, *Anal. Chem.* (1988) 60, 1318–1323.
- Fan, T. Characterization of naphthenic acids in petroleum by fast atom bombardment mass spectrometry, *Energy and Fuels* (1991) 5, 371–375.
- Fukui, Y., and Yuu, S. Measurement of the charge on small gas bubbles, *AIChE J.* (1982) 28, 866–868.

- Hupka, J., and Miller, J.D. Electrophoretic characterization and processing of Asphalt Ridge and Sunnyside tar sands, *Inter. J. Mineral Processing* (1991) 31, 217–231.
- Kubota, K., Hayashi, S., and Inaoka, M. A convenient experimental method for measurement of zeta-potentials generated on the bubble suspended in aqueous surfactant solutions, *J. Colloid and Interface Sci.* (1983) 95, 362–369.
- Laskowski, J.S., Yordan, J.L., and Yoon, R.H. Electrokinetic potential of microbubbles generated in aqueous solutions of weak electrolyte type surfactants, *Langmuir* (1989) 5, 373–376.
- Leja, J., and Bowman, C.W. Application of thermodynamics to the Athabasca tar sands, *Can. J. Chem. Eng.* (1969) 46, 479–481.
- Li, C., and Somasundaran, P. Reversal of bubble charge in multivalent inorganic salt solutions — effect of magnesium, *J. Colloid and Interface Sci.* (1991) 146, 215–218.
- McConaghy, D.C., Paradowski, E.W., and Porteous, K.C., unpublished results from research at Syncrude, 1973.
- Misra, M., Aguilar, R., and Miller, J.D. Surface chemistry features in the hot water processing of Utah tar sand, *Separation Science and Technology* (1981) 16 1523–1544.
- Moschopedis, S.E., Fryer, J.F., and Speight, J.G. Water-soluble constituents of Athabasca bitumen, *Fuel* (1977) 56, 109–110.
- Moschopedis, S.E., Schulz, K.F., Speight, J.G., and Morrison, D.N. Surface-active materials from Athabasca oil sands, *Fuel Proc. Technol.* (1980) 3, 55–61.
- Okada, K., and Akagi, Y. Method and apparatus to measure zeta potential of bubbles, *J Chem. Eng. Japan* (1987) 20, 11–15.
- Okada, K., Akagi, Y., and Yoshioka, N. Effect of zeta potential of oil droplets and bubbles on flotation of oil-in-water mixtures, *Can. J. Chem. Eng.* (1988) 66, 276–281.

- Okada, K., Akagi, Y., Kogure, M., and Yoshioka, N. Effect of surface charges of bubbles and fine particles on air flotation process, *Can. J. Chem. Eng.* (1990) 68, 393–399.
- Pasternack, D.S., and Clark, K.A. The components of the bitumen in Athabasca bituminous sand and their significance in the hot water separation process, Research Council of Alberta (1951) Report No. 58, 14pp.
- Sanford, E.C., and Seyer, F.A. Processibility of Athabasca tar sand using a batch extraction unit: the role of NaOH, *CIM Bulletin* (1979) 72, 164–169.
- Sanford, E.C. Processibility of Athabasca oil sand: Interrelationship between oil sand fine solids, process aids, mechanical energy and oil sand age after mining, *Can. J. Chem. Eng.* (1983) 61, 554–567.
- Schramm, L.L., Smith, R.G., and Stone, J.A. A surface tension method for the determination of anionic surfactants in hot water processing of Athabasca oil sands, *Colloids and Surfaces* (1984a) 11, 247–263.
- Schramm, L.L., Smith, R.G., and Stone, J.A. The influence of natural surfactant concentration on the hot water process for recovering bitumen from the Athabasca oil sands, *AOSTRA J. Res.* (1984b) 1, 5–13.
- Schramm, L.L., and Smith, R.G. The influence of natural surfactants on interfacial charges in the hot-water process for recovering bitumen from the Athabasca oil sands, *Colloids and Interfaces* (1985) 14, 67–85.
- Schramm, L.L., Smith, R.G., and Stone, J.A. On the processibility of mixtures of oil sands, *AOSTRA J. Res.* (1985) 1, 147–161.
- Schramm, L.L., and Smith, R.G. Two classes of anionic surfactants and their significance in hot water processing of oil sands, *Can. J. Chem. Eng.* (1987a) 65, 799–811.
- Schramm, L.L., and Smith, R.G. Some observations on the aging phenomenon in the hot water processing of Athabasca oil sands. Part 1. The nature of the phenomenon, *AOSTRA J. Res.* (1987b) 3, 195–213.



- Schramm, L.L., and Smith, R.G. Some observations on the aging phenomenon in the hot water processing of Athabasca oil sands. Part 2. The mechanism of aging, *AOSTRA J. Res.* (1987c) 3, 215–223.
- Schramm, L.L., and Smith, R.G. Some parametric studies of oil sand conditioning in the hot water flotation process, *AOSTRA J. Res.* (1989) 5, 87–107.
- Smith, R.G., and Schramm, L.L. Processibility of Athabasca oil sand by the hot-water process when contaminated with overburden material, *Fuel Proc. Technol.* (1989) 23, 215–231.
- Speight, J.G., and Moschopedis, S.E. Factors affecting bitumen recovery by the hot water process, *Fuel Proc. Technol.* (1977/1988) 1, 261–268.
- Srinivasan, N.S., Spitzer, J.J., and Hepler, L.G. Electrophoretic properties of oil sands tailings and constituent clays in aqueous suspensions, *J. Can. Petr. Techn.* (1982, July–August), 25–30.
- Takamura, K. Microscopic structure of Athabasca oil sand, *Can. J. Chem. Eng.* (1982) 60 538–545.
- Wallace, D., and Henry, D. Aging of oil sand during storage, Preprint, Engineering Foundation Conference on the Processing of Energy; Minerals: Shale, Tar Sands and Coal. Henniker, New Hampshire, August 19–24 (1984) 14pp.
- Wallace, D., Henry, D., and Takamura, K. A physical chemical explanation for deterioration in the hot water processibility of Athabasca oil sand due to aging, *Fuel Sci. Technol. Int.* (1989) 7, 699–725.
- Yoon, R., and Yordan, J.L. Zeta-potential measurements on microbubbles generated using various surfactants, *J. Colloid and Interface Sci.* (1986) 113, 430–438.

# 6

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## *Fate of Sodium Hydroxide in the Hot Water Process*



## **INTRODUCTION**

The hot water process, when used to process an average grade oil sand (10–11% bitumen), typically uses 0.15 g NaOH/kg oil sand or 3.75 meq/kg of oil sand. When the process water (after clean up by ultrafiltration) is titrated with standard hydrochloric acid, there is found only a very small amount of a basic species at  $\text{pH} \approx 8.0$  along with a much greater amount of basic species with an end point at  $\text{pH} \approx 4.5$ . It appears that the material neutralized at  $\text{pH} \approx 8.0$  is carbonate while the material neutralized at  $\text{pH} \approx 4.5$  is bicarbonate plus sodium carboxylate surfactant. The evidence that this is the case was obtained by acidifying the sample to  $\text{pH} \approx 3.0$  with hydrochloric acid to convert carbonate and bicarbonate to carbonic acid followed by degasification with nitrogen to drive off carbon dioxide. The sample was then restored to the original pH and again titrated with standard hydrochloric acid. This titration showed only a very small amount of material at an end point of  $\text{pH} \approx 5.0$  which is believed to be sodium carboxylate surfactant. It appears that most, if not all, of the sodium hydroxide is consumed during the process, but only about 0.25 meq of sodium carboxylate surfactant are produced per kg oil sand. The fate of the missing sodium hydroxide is of interest in developing an understanding of the mechanism of the process. The experimental work described in this chapter was carried out to elucidate the chemistry of the reaction(s) that occur between sodium hydroxide and oil sand components.

## **Experience from Reservoir Floods with Sodium Hydroxide**

Sodium hydroxide flooding of oil reservoirs has received attention over many years because sodium hydroxide is able to reduce interfacial tension between oil and reservoir rock to very low values, thereby facilitating oil flow from the reservoir. The process is inefficient because sodium hydroxide is consumed by reservoir rock and quickly becomes unavailable for reduction of interfacial tension. The reactions which consume sodium hydroxide have been studied, with the evidence pointing to reaction of the sodium hydroxide with clays and other minerals.

Clays and other reservoir minerals have been studied over the years with experience indicating that no two reservoirs have the same mineral composition. Clays that have been identified include kaolinite, montmorillonite, illite, feldspar, and

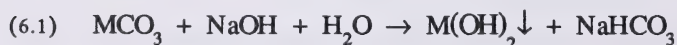


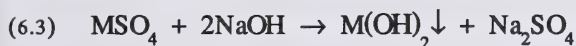
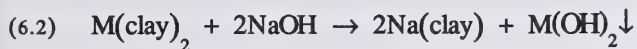
chlorite. Other minerals that have been identified include silica, dolomite, zeolite, calcite, siderite, gypsum, and pyrite.

Reactivity of sodium hydroxide with specific clays and minerals has also been studied. Holm and Robertson (1981) tested both sodium and calcium forms of kaolinite, illite, and montmorillonite with a 0.7 wt% solution of sodium orthosilicate by shaking the clay with a sodium orthosilicate solution for 5 days at room temperature. The sodium clays consumed very little of the orthosilicate while the calcium clays consumed the same number of moles of orthosilicate as the total number of moles of exchangeable calcium. The authors suggested that the calcium on the clay is exchanged for sodium and precipitated from solution as calcium silicate or calcium hydroxide. Siderite was also tested (very reactive) as were dolomite (moderately reactive) and calcite (unreactive) by the same test method. The reactivity of siderite was explained as due to reaction between siderite and sodium orthosilicate to form insoluble iron silicate and soluble sodium carbonate. Failure of calcite to react by the same mechanism was expected since calcium carbonate is less soluble than calcium silicate.

In a second study by Mohnot and Bae (1989), kaolinite, gypsum, montmorillonite, illite, dolomite, and zeolite were identified as very reactive to sodium hydroxide under reservoir conditions. Reservoir conditions were simulated by heating samples of the minerals with 5 wt% sodium hydroxide at 82°C. Feldspar and chlorite were identified as moderately reactive while calcite and quartz sand were reported to be unreactive. The study used commercial clays and no attempt was made to differentiate between sodium forms and divalent forms of the clays. It is probable that the clays used were mixtures of the sodium, calcium, and magnesium forms.

The two references cited above suggested that consumption of sodium hydroxide by reservoir rock is due to reaction of the sodium hydroxide with divalent clays such as calcium and magnesium kaolinite and illite, divalent carbonates such as siderite and divalent sulfates such as gypsum. The reactions described below are suggested where M is Ca, Mg, or Fe.





It seems probable that minerals in oil sands can react in ways that are similar to reactions in petroleum reservoirs and that conditions for the hot water process (82°C) are similar to conditions expected in some underground reservoirs. Consequently, the possibility that sodium hydroxide consumption in the hot water process is via reaction with divalent clays, carbonates, and sulfates was investigated.

### Evidence for Divalent Minerals in Oil Sand

Typical x-ray diffraction analysis results for oil sand solids (both the coarse solids fraction and the fines fraction were analyzed and the data were combined to give an oil sands solids analysis) are collected in the Table 6.1 given below:

*Table 6.1.*

Component	Quantity (%)
Quartz	82
K-feldspar	5
Calcite	Trace
Dolomite	nil
Siderite	Trace
Pyrite	nil
Kaolinite	4
Illite	7
Chlorite	1
Smectite	Trace
Mixed layer clays	1
Anhydrite	Trace

The analysis reveals the presence of clays, particularly kaolinite and illite, but does not reveal how much of these clays are in the divalent metal form. The analysis was unable to detect pyrite in the sample either because the quantity present was below the detection limit or indeed, not present in the sample. The exchangeable cations in clean clay solids as isolated from oil sands have been determined (Baptista, 1989). In that study the clean clay fractions were obtained by extracting bitumen from the oil sands with toluene and allowing the coarse fraction of the clean solids to settle in water. The clay fraction was then isolated from the water by centrifugation. The exchangeable cations in the clay fraction were determined by exchange with potassium chloride and magnesium chloride and were found to include sodium, calcium, magnesium, and potassium. The results are tabulated below in Table 6.2.

**Table 6.2.** Milliequivalents/kg of clay

Cation	Sample 1	Sample 2	Sample 3	Sample 4
Na	74	119	326	450
Ca	178	132	45	20
Mg	64	94	27	15
K	89	33	29	30

The data show significant quantities of calcium and magnesium in the clay fractions from the samples.

The x-ray diffraction data show the presence of traces of siderite and calcite and the presence of siderite has been confirmed by other studies (Kotlyar, Sparks, and Kodama, 1984, and Mikula, Munoz, and Lam, 1989). The quantities of these minerals appear to be relatively small and cannot be determined by x-ray diffraction. However, there is little doubt that divalent carbonate minerals are present, and since the amount of sodium hydroxide used in the hot water process is relatively small there may be enough carbonate present to consume a significant fraction of the sodium hydroxide.

Evidence for the presence of divalent sulfates was obtained by extracting a low grade (8.4% bitumen) oil sand with hot water according to the procedure described in the experimental section of this chapter. The water extract in this case contained relatively large quantities of sulfate, calcium, and magnesium ions,

indicating the presence of calcium and magnesium sulfate. This oil sand was unusual since in most cases water extracts of oil sands contain only a small amount of sulfate and no calcium or magnesium. Studies of oil sand aging described in the previous chapter have confirmed the presence of ferric sulfate, which increases in concentration as oil sands age on storage at room temperature in the presence of air.

### **Evidence for the Involvement of Divalent Cations**

If sodium hydroxide is being consumed by reaction with divalent clays, carbonates, and sulfates, then it becomes unavailable for reaction with bitumen components for the production of carboxylate surfactants. It is also possible that the divalent compounds are reacting to precipitate carboxylate surfactants as divalent metal carboxylates. The addition of a chelating agent would be expected to lead to binding of the divalent compounds, reducing the amount of sodium hydroxide needed for maximum primary recovery (and needed to yield the critical surfactant concentration). To test this idea, an oil sand was processed in the Syncrude batch extraction unit first with sodium hydroxide alone (various concentrations) and then with sodium ethylenediamine tetraacetate (EDTA) and sodium hydroxide (various concentrations). With sodium hydroxide alone, the oil sand needed 15.0 meq of sodium hydroxide per kg of oil sand to reach the critical carboxylate surfactant concentration and optimum primary recovery and the process water was found to contain sodium as the only cation. The use of sodium ethylenediamine tetraacetate reduced the sodium hydroxide requirement to 10.0 meq per kg of oil sand and the process water was found to contain iron, calcium, and magnesium in addition to sodium. The number of moles of divalent metal in solution was almost equivalent to the moles of EDTA used in the experiment.

The reduction in the amount of sodium hydroxide needed for maximum primary recovery when sodium ethylenediamine tetraacetate was used is considered strong evidence that divalent metal compounds are present in oil sands and that such compounds react with (consume) sodium hydroxide.



## **EXPERIMENTAL**

### **Oil Sand Samples**

Oil sand samples were obtained from Syncrude's mine site as freshly mined 20 kg samples. The oil sand was homogenized by chopping to a size smaller than 1 mm by using the edge of a 6 inch spatula and mixing the chopped material in a large polyethylene bag. The homogenized samples were then transferred to polyethylene pails and placed in storage at  $-30^{\circ}\text{C}$  with samples removed from storage as required and used after warming to room temperature (one hour).

### **Hot Water Extraction of Oil Sands**

A sample of oil sand (100 g) was placed in a 400 mL beaker and 100 mL of boiling water was added. The mixture was stirred for about one minute with a glass stirring rod and the resulting slurry was allowed to stand for a further four minutes. During this time the sand settled to the bottom of the beaker and at the end of the total five minutes the aqueous layer was decanted. This layer was then clarified by centrifugation (15,000 rpm for 30 minutes), followed by ultrafiltration (Amicon Diaflow YM5, 5000 MW nominal pore size).

### **Batch Extractions**

The standard procedure described in Appendix 3 was used. The secondary tailings were clarified by the same procedure of centrifugation and ultrafiltration described above under **Hot Water Extraction of Oil Sands**. Secondary tailings bitumen and solids were recovered from the centrifuge tubes and filters by washing with toluene and water and the amounts of oil and solids recovered were determined by oil, water, solids analysis. Oil determinations were carried out on the primary, secondary, and wall froths as well as on the primary and secondary tailings. Primary and secondary recoveries were calculated as a percentage of the total recovered oil.

### **Batch Extraction with Sodium Ethylenediamine Tetraacetate**

An oil sand containing 11.4 wt% bitumen was processed in the Syncrude batch extraction unit using various quantities of sodium hydroxide ranging from zero to 20 meq/kg of oil sand and in each case using 2.30 meq of sodium tetraethylenediamine tetraacetate/kg of oil sand. The secondary tailings were clarified as described in the procedure for **Batch Extractions** and the clarified material was analyzed for sodium, calcium, magnesium, and iron by inductively coupled plasma emission spectroscopy. The sample was found to contain 1.40 meq iron/kg of oil sand, 1.26 meq calcium/kg and 0.28 meq magnesium/kg for a total of 2.94 meq  $M^{2+}$ /kg oil sand. Optimum primary recovery occurred at 10.0 meq NaOH/kg oil sand and the amount of carboxylate surfactant in the water from this experiment was 0.12 meq/L of tailings water.

### **Analysis of Aqueous Streams for Anionics**

Clarified samples either from hot water extraction of oil sands or from batch extractions were analyzed for carbonate and the total of bicarbonate plus sodium carboxylate surfactant by titration of 10 g samples with standard 0.006 N hydrochloric acid. The titration was carried out using a Mettler DL20 autotitrator and using the first derivative of the titration curves to determine end points. The titration curve had two end points, one at  $pH \approx 8.0$  and the other at  $pH \approx 4.5$ ; the end point at  $\approx 8.0$  was taken as due to carbonate while the end point at  $\approx 4.5$  was taken as due to bicarbonate plus sodium carboxylate surfactant. The samples were also analyzed for sulfate and chloride by ion chromatography and for carboxylate surfactant by the surface tension method described in Chapter 3. Bicarbonate was calculated from the total of bicarbonate plus carboxylate surfactant by subtracting any contribution from carbonate and the value for carboxylate surfactant as determined by surface tension titration.

### **Analysis of Aqueous Streams for Cationics**

Aqueous streams, after clarification according to the procedure given above for batch extractions, were analyzed for metallic species (including Na, Fe, Ca, Mg and K) by inductively coupled plasma atomic emission spectroscopy.

## **RESULTS AND DISCUSSION**

### **Reaction Products from Oil Sand and Sodium Hydroxide**

Experience with the procedure described in the experimental section of this chapter on hot water extraction of oil sands has shown that most oil sands yield aqueous extracts containing only carbonate (a very small amount), bicarbonate, sulfate (again a very small amount), chloride, with sodium as the only significant cation. However, a few oil sands yield aqueous extracts that also contain calcium and magnesium and unusually large concentrations of sulfate.

Normal oil sands (the bulk of oil sands which do not contain soluble calcium and magnesium) would, according to equations 6.1 through 6.3, be expected to react with sodium hydroxide to produce carbonate/bicarbonate and sodium ions. These oil sands would also be expected to produce sulfonate and carboxylate surfactants when treated with sodium hydroxide. The carbonate/bicarbonate species would be expected from equation 6.1 involving reaction of sodium hydroxide with divalent carbonates. Reaction according to equation 6.2 would be expected to produce only insoluble materials (sodium clays and divalent hydroxide) while equation 6.3 would not be involved since oil sands, referred to as normal, do not contain soluble divalent sulfates. A net loss of ionic species would be expected because some of the added sodium hydroxide converts to insoluble products when reacted as in equation 6.2.

The above predictions were tested by treating an oil sand containing 10.5% bitumen with concentrations of sodium hydroxide ranging from zero to 20 meq/kg of oil sand. The clarified process water was analyzed for anions and cations according to the procedure given in the experimental section of this chapter with the anion results listed in Table 6.3. The data in the column labelled "Loss" represent the loss of anionic species that occurred, assuming that the reaction of sodium hydroxide with oil sand should produce anionic species equal to the production of anionic species in the blank experiment (zero sodium hydroxide) plus that added in the form of sodium hydroxide.

**Table 6.3.** *Quantity of anionic species (meq/kg of oil sand)*

NaOH	$\text{CO}_3^{2-}$	$\text{HCO}_3^-$	$\text{SO}_4^{2-}$	$\text{Cl}^-$	$\text{RCOO}^-$	Total	Loss
0	0.28	5.98	1.26	1.28	0.04	8.84	
15	0.84	11.68	1.36	1.08	0.24	15.20	8.6
20	3.96	11.64	0.92	1.18	0.32	18.02	10.8

The data in Table 6.3 confirm the predictions that the added hydroxide will be converted to carbonate/bicarbonate. There was a significant loss of anionic species in agreement with equation 6.2, which calls for precipitation of hydroxide as insoluble divalent hydroxide.

The analytical results for cations are given in Table 6.4.

**Table 6.4.** *Quantity of cationic species (meq/kg of oil sand)*

NaOH	$\text{Na}^+$	$\text{Fe}^{2+}$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{K}^+$	Total	Loss
0	9.32	0	0.12	0.16	0.30	9.90	
15	16.26	0	0	0	0.18	16.44	8.5
20	19.80	0	0	0	0.20	20.00	9.9

The column labelled "Loss" in Table 6.4 was calculated in the same way as the "Loss" column in Table 6.3. The data in Table 6.4 confirm the prediction that there would be some loss of sodium since equation 6.2 calls for conversion of divalent clays to insoluble sodium clay with precipitation of the displaced divalent cation as divalent hydroxide. The three experiments had reasonable agreement between total anionic species and total cationic species although there was in all cases an excess of cationic species of about 10%. The excess is believed to be due to measurement errors, particularly in the sodium measurement, rather than to missing species. There was good agreement between the anionic loss and the cationic loss.

An abnormal oil sand (one containing soluble calcium and magnesium and a high concentration of sulfate) was also processed with sodium hydroxide and the process water was analyzed for ionic species. The expectation was that reaction 6.1 would still act to produce carbonate/bicarbonate and reaction 6.2 would continue to reduce the amount of ionic species by precipitating sodium as sodium clay and



hydroxide as divalent hydroxides while reaction 6.3 would act to precipitate calcium and magnesium as either the hydroxides or carbonates and cause a disappearance of calcium and magnesium. No change would be expected in sulfate concentration and the anionic loss would be expected to equal the cationic loss. The analytical data for anionic species are recorded in Table 6.5.

**Table 6.5.** *Quantity of anionic species produced (meq/kg of oil sand)*

NaOH	$\text{CO}_3^{2-}$	$\text{HCO}_3^-$	$\text{SO}_4^{2-}$	$\text{Cl}^-$	$\text{RCOO}^-$	Total	Loss
0	0.40	2.36	8.26	0.06	0	11.08	
20	0.56	7.62	8.04	0.14	0.06	16.42	14.7
50	15.64	11.94	7.16	0.02	0.28	35.04	26.0
60	20.86	13.54	8.68	0.04	0.32	43.44	27.6

The data confirm the predictions: there was an increase in carbonate/bicarbonate with increasing sodium hydroxide and there was no change in sulfate. A loss of anionic species occurred which seems to have reached a maximum at about 50 meq/kg of sodium hydroxide.

The analytical results for the same experiments for cationic species are given in Table 6.6.

**Table 6.6.** *Quantity of cationic species produced (meq/kg of oil sand)*

NaOH	$\text{Na}^+$	$\text{Fe}^{2+}$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{K}^+$	Total	Loss
0	2.18	0.02	3.94	4.78	0.72	11.74	
20	17.40	0	0.26	0.20	0.30	18.16	13.6
50	37.94	0	0.18	0	0.24	38.36	23.4
60	46.00	0	0.20	0	0.24	46.44	25.3

The cationic data also confirm the predictions: there was a disappearance of calcium and magnesium along with the predicted increase in sodium. The total cationic species found were again about 10% greater than the total of anionic species (judged to be due to analytical error) and the loss of anionic species was about equal to the loss of cationic species.

### **Reaction Products with Added Divalent Carbonates**

The data already presented are entirely consistent with the presence of divalent carbonates in oil sand and with their reaction with sodium hydroxide to convert insoluble divalent carbonate to soluble sodium carbonate/bicarbonate and insoluble divalent hydroxide. This reaction makes sodium hydroxide unavailable for production of carboxylate surfactants and is expected to lead to low primary recoveries. Additional evidence for the role played by divalent carbonates was sought by studying the reaction of oil sand with added carbonates.

The carbonates studied include sodium carbonate, calcium carbonate, magnesium carbonate, and iron (ferrous) carbonate. All of these compounds were used in the amount of 2.0 g  $\text{MCO}_3/\text{kg}$  of oil sand and they were added to the batch reactor along with the oil sand. Experiments were carried out using an oil sand containing 10.2 wt% bitumen which, when processed at standard conditions, required 0.20 g NaOH/kg oil sand (5.0 meq NaOH/kg of oil sand) to yield maximum primary recovery of 82%.

Reactions 6.1 through 6.3 can be used as a basis for predicting the behavior of the divalent carbonates. Since there will now be more divalent carbonate available, the expectation is that more of the sodium hydroxide will react via reaction 6.1. There should then be more carbonate/bicarbonate produced and less free carboxylate surfactant (because there will be less sodium hydroxide available to react with carboxylic acids in the bitumen). The production of less free carboxylate surfactant would be expected to result in a reduced primary recovery. Detection of increased carbonate/bicarbonate is not expected to be possible in the experiments under consideration due to the use of excess carbonate as the additive.

All the experiments were performed using 5.0 meq NaOH/kg of oil sand. Recovery and froth quality data are given in Table 6.7 where 1°R is primary recovery, %o is %oil, %w is % water, and %s is % solids

Table 6.7.

Additive	1°R	2°R	Primary froth			Secondary froth		
			%o	%w	%s	%o	%w	%s
None	82	13	63	30	7	24	53	24
Na <sub>2</sub> CO <sub>3</sub>	81	11	71	20	8	37	40	23
CaCO <sub>3</sub>	72	20	61	33	6	24	51	25
MgCO <sub>3</sub>	13	52	36	61	3	11	79	10
FeCO <sub>3</sub>	81	16	62	31	8	27	50	23

Sodium carbonate had little, if any, effect on primary recovery although it did increase the bitumen content of the primary froth from 63% in the case where no additive was used to 71%. This result is not unexpected because it is known that sodium carbonate can function as a process additive in a way very similar to sodium hydroxide. In this case the amount of sodium hydroxide used was optimum so the addition of extra basic material would be expected to either reduce primary recovery slightly or, as in many cases, have no significant effect.

Calcium carbonate had a small effect on primary recovery while magnesium carbonate had a relatively large effect and iron carbonate had no effect. Magnesium carbonate also reduced the bitumen content of the primary froth while calcium carbonate and iron carbonate had no effect on froth quality.

Anionic species in the process water from the experiments were measured and the data are recorded in Table 6.8.

Table 6.8. Quantity of anionic produced (meq/kg oil sand)

NaOH	CO <sub>3</sub> <sup>2-</sup> added meq/kg	CO <sub>3</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	RCOO <sup>-</sup>	Total
None		0	8.22	0.44	0.28	0.24	9.26
Na <sub>2</sub> CO <sub>3</sub>	18.9	6.00	23.30	0.30	0.14	0.22	30.00
CaCO <sub>3</sub>	20.0	0.32	8.22	0.48	0.28	0.12	9.56
MgCO <sub>3</sub>	23.8	1.02	12.88	0.54	0.32	0.04	14.98
FeCO <sub>3</sub>	17.2	0	8.54	0.22	0.12	0.24	9.12

Sodium carbonate had almost no effect on the quantity of free carboxylate surfactant and its lack of effect on primary recovery is understandable. It is normal for quantities of process aid beyond the amount needed to produce the critical concentration to result in a free carboxylate surfactant concentration greater than the critical concentration. However, instances have been found where this was not so, with extra process aid having no further effect on free carboxylate surfactant concentration. It appears this oil sand is one such case. The total anionic species found in the process water (30.0 meq/kg) was close to the total of anionic species produced in the experiment without additive plus the added carbonate (28.2).

Calcium carbonate caused a considerable reduction in the amount of free carboxylate surfactant, which accounts for the reduction in primary recovery. This effect must be due to precipitation of carboxylate surfactants by calcium ions because calcium carbonate is not expected to react with sodium hydroxide due to the fact that calcium carbonate is less soluble in water than calcium hydroxide. There was a total of 29.3 meq anionic species/kg of oil sand possible in the calcium carbonate case but only 9.6 meq/kg were found in the produced water. This may be due to the low solubility of calcium carbonate, which probably dissolves only to a slight extent under the reaction conditions.

Magnesium carbonate reduced the amount of free carboxylate surfactant to a very low concentration and the very low primary recovery was the result. There was a total of 33.1 meq/kg of anionic species possible in the magnesium carbonate case if all the magnesium carbonate dissolves but only 14.8 meq/kg recovered. Again the discrepancy is probably due to the low solubility of magnesium carbonate under the reaction conditions.

Iron carbonate had no effect on the amount of free carboxylate surfactant, which accounts for the previous finding that it had no effect on primary recovery. In this case the total amount of possible anionic species was 26.5 meq, and the amount found was 9.12 meq, again believed due to the low solubility of iron carbonate.

Cationic species were also measured for the experiments with added carbonates with the data given in Table 6.9.



**Table 6.9.** *Quantity of cationic species produced (meq/kg oil sand)*

Additive	Sodium added meq/kg	Na <sup>+</sup>	Fe <sup>2+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	K <sup>+</sup>	Total
None		8.56	0	0.08	0	0.32	8.96
Na <sub>2</sub> CO <sub>3</sub>	18.9	38.80	0	0.04	0	0.28	39.12
CaCO <sub>3</sub>	20.0	10.14	0	0.16	0	0.38	10.68
MgCO <sub>3</sub>	23.8	13.16	0	0.54	4.64	0.80	19.14
FeCO <sub>3</sub>	17.2	8.64	0.02	0.04	0	0.32	9.02

The quantities of cationic species are equal to the anionic quantities, with, however, poor agreement for the sodium carbonate and magnesium carbonate cases. In the sodium carbonate case it appears that the cationic measurement is the one in error because the total found of 39.12 meq cationic species/kg of oil sand exceeds the total expected of 27.9 meq/kg.

Calcium carbonate and magnesium carbonate appear to be soluble enough and reactive enough to interfere with the hot water process. Both materials act to reduce the amount of free carboxylate surfactant, which in turn causes a reduction in primary recovery if the process is operated at a constant amount of sodium hydroxide. Iron carbonate appears to have no effect, probably because of its very low solubility.

### Reaction Products with Added Divalent Sulfates

The sulfates studied included sodium sulfate, calcium sulfate, magnesium sulfate, and ferrous sulfate. All of these were used in the amount of 2.0 g of metal sulfate/kg of oil sand and the batch extraction experiments were carried out using the oil sand containing 10.2% bitumen with 5.0 meq NaOH/kg of oil sand. The oil sand was the same as was used in the study of carbonates described above and as indicated it gave maximum primary recovery of 82% when treated with 5.0 meq NaOH/kg of oil sand.

The divalent sulfates were expected to react with sodium hydroxide via reaction 6.3 to convert the divalent sulfate to sodium sulfate and divalent hydroxide

(which would be expected to precipitate). One of the expected results of the reaction would be a net decrease in ionic species. The reaction would also be expected to decrease the amount of sodium hydroxide available to make carboxylate surfactant and result in low carboxylate surfactant concentrations and low primary recoveries. A reduction in the amount of carbonate/bicarbonate produced was also expected because with more sodium hydroxide reacting via reaction 6.3, there would be less available to react via reaction 6.1.

Recovery and froth analysis results for the experiments are summarized in Table 6.10.

*Table 6.10.*

Additive	1°R	2°R	Primary froth			Secondary froth		
			%o	%w	%s	%o	%w	%s
None	82	13	63	30	7	24	53	24
Na <sub>2</sub> SO <sub>4</sub>	60	31	56	40	5	40	42	19
CaSO <sub>4</sub>	22	35	35	61	4	15	77	8
MgSO <sub>4</sub>	17	23	27	68	4	12	80	8
FeSO <sub>4</sub>	5	26	12	84	4	8	84	8

All of the sulfates reduced primary recovery, although the reduction by sodium sulfate was not as great as the reduction caused by the divalent sulfates. The reduction by sodium sulfate was surprising because it would not be expected to react with sodium hydroxide or cause a reduction in the concentration of carboxylate surfactant. The phenomenon may be a salt effect of some so far undefined nature because other salts such as sodium chloride cause similar reductions in primary recovery. The sulfates also reduced the bitumen content of primary froth. All of the sulfates, except sodium sulfate, reduced the bitumen content of secondary froth.

Ferrous sulfate was more detrimental, as far as primary recovery is concerned, than the other sulfates and it is interesting to speculate on the reasons for this. It may be that the ferrous sulfate reacts, like the other sulfates, with sodium hydroxide to, in this case, form ferrous hydroxide. The ferrous hydroxide would be expected to easily oxidize to ferric hydroxide under the experimental conditions and it is possible that ferric oxide is very effective at removing carboxylate surfactant from solution.

Anionic species in the process water from the experiments were also measured and the data are given in Table 6.11.

**Table 6.11.** *Quantity of anionic species produced (meq/kg oil sand)*

NaOH	$\text{CO}_3^{2-}$ added meq/kg	$\text{CO}_3^{2-}$	$\text{HCO}_3^-$	$\text{SO}_4^{2-}$	$\text{Cl}^-$	$\text{RCOO}^-$	Total
None		0	8.22	0.44	0.28	0.24	9.26
$\text{Na}_2\text{SO}_4$	28.2	0.16	6.62	30.16	0.28	0.16	37.42
$\text{CaSO}_4$	29.4	0.20	1.38	27.80	0.28	0.10	30.50
$\text{MgSO}_4$	33.4	0.02	1.78	34.20	0.30	0.06	36.38
$\text{FeSO}_4$	26.4	0	0.18	29.76	0.28	0	30.26

Sodium sulfate reduced the amount of free carboxylate surfactant from 0.24 meq surfactant/kg of oil sand to 0.16 meq/kg, which accounts for the observed reduction in primary recovery. There does not at this time appear to be an easy explanation for the phenomenon. The total of anionics (mainly sulfate) for the experiment of 37.42 meq/kg was close to the total (37.46 meq/kg) of anionics produced in the reference experiment (no additive) plus the amount of sulfate added as sodium sulfate.

Calcium sulfate reduced the amount of free carboxylate surfactant and also reduced the concentration of bicarbonate ion. Both reductions agree with the predictions made according to reactions 6.1 to 6.3. The total anionic species found in the produced water of 30.3 meq anionic/kg of oil sand was less than the possible quantity (38.7 meq/kg), in agreement with the prediction that a loss of ionic species would occur.

Magnesium sulfate also reduced free carboxylate surfactant and bicarbonate ion concentrations in accord with the predictions. The total anionic species found in the produced water of 36.4 meq anionics/kg of oil sand was less than the possible quantity of 42.7 meq/kg, again in agreement with the expectation that a loss of ionic species would occur.

Ferrous sulfate also acted to reduce the concentration of free carboxylate surfactant and bicarbonate ion. Total anionic production was also less than the possible amount, again in agreement with the prediction.

Cationic species were also measured for the experiments and the results are compiled in Table 6.12.

**Table 6.12.** *Quantity of cationic species produced (meq/kg oil sand)*

Additive	Sodium added	Na <sup>+</sup>	Fe <sup>2+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	K <sup>+</sup>	Total
None		8.56	0	0.08	0	0.32	8.96
Na <sub>2</sub> SO <sub>4</sub>	28.2	42.06	0	0.46	0	0.68	43.74
CaSO <sub>4</sub>	29.4	14.30	0	19.78	3.34	0.88	38.2
MgSO <sub>4</sub>	33.4	14.60	0	2.72	26.34	1.02	44.68
FeSO <sub>4</sub>	26.4	14.08	2.08	4.56	5.70	0.92	27.90

The cation data for sodium sulfate showed a total of 43.7 meq/kg of cationics produced, which compares with the total 37.4 meq/kg of anionics. The only cation in any significant quantity was sodium. The calcium sulfate experiment produced 38.3 meq cationics/kg of oil sand (38.5 meq/kg of anionics), which consisted mainly of sodium and calcium, with a small amount of magnesium. It may be that there was some ion exchange between calcium sulfate and magnesium clays. The magnesium sulfate experiment produced 44.7 meq cationic species/kg of oil sand (36.4 meq/kg of anionics) with the cations consisting mainly of sodium and magnesium ions with less calcium. Again, ion exchange with calcium clays may be taking place. The ferrous sulfate experiment produced 27.9 meq/kg of total cationic species (30.3 meq/kg of anionics). Here the produced cations were sodium, calcium, magnesium, and iron, indicating perhaps again ion exchange between the iron sulfate and calcium and magnesium clays. Agreement between total anionics and total cationics was reasonable, but some disagreements were as large as 20%. This disagreement is believed due to experimental errors, particularly in the sodium and sulfate measurements. The quantity of added sulfate for the experiments is given in Table 6.11 and it would be expected that this quantity would agree with the quantity measured because all the sulfates used are water soluble. The measured quantities are close to the input quantities but errors of as much as  $\pm 10\%$  did occur in some cases. This error along with the previously discussed 10% error in the sodium measurements can account for the 20% error sometimes noted.



All of the divalent sulfates acted to reduce the amount of free carboxylate surfactant, which in turn caused large reductions in primary recovery. The sulfates were more deleterious than the corresponding carbonates, with ferrous sulfate having the largest effect on the process. The detailed experimental results agree with the proposal that sulfates that may be present in oil sand interfere with the hot water process either because they act to consume sodium hydroxide or because they act to precipitate carboxylate surfactant or, perhaps because both mechanisms are operative.

### **Reaction Products with Added Divalent Clays**

Calcium illite and calcium kaolinite were selected as representative of divalent clays and samples were prepared from commercial samples of sodium illite and sodium kaolinite according to the procedure of Ferris and Jepson (1975). The exchangeable cation content of the clays was determined using a method described by Schramm (1980) involving exchange of the clay cations with ammonium acetate solution and determination of the cation content of the exchange solution by inductively coupled plasma atomic emission spectroscopy. The calcium illite had 27.3 meq  $\text{Ca}^{2+}/100$  g of clay and 7.60 meq  $\text{Na}^+/100$  g of clay. The calcium kaolinite had 9.0 meq  $\text{Ca}^{2+}/100$  g of clay and 8.1 meq  $\text{Na}^+/100$  g of clay. Conversion to the calcium forms was not complete but these are realistic compositions and were expected to provide a valid test of the effect of calcium clays on the hot water process.

A rich oil sand (13.6 wt% bitumen) was used to study the effect of the calcium clays. This oil sand gave 90% primary recovery in the blank experiment (zero sodium hydroxide) and the free carboxylate surfactant in this experiment was 0.24 meq/kg of oil sand (0.12 meq/L in the water). Such behavior is fairly typical of rich oil sands which often yield maximum primary recovery at zero sodium hydroxide and contain carboxylate surfactant at the critical concentration in produced water. It was desired, however, to study the effect of the calcium clays using sodium hydroxide; consequently the experiments with the clays were carried out using 0.10 g NaOH/kg oil sand. At this level the oil sand without clay addition gave 49% primary recovery and there were 0.44 meq carboxylate surfactant/kg of oil sand (0.20 meq/L in the water). This amount of surfactant is well above the critical amount and accounts for the low primary recovery.

Experiments with the calcium clays with the rich oil sand were conducted initially using 2.0 g of clay/kg of oil sand and increased primary recoveries resulted. The increased recoveries were thought to be due to a reduction in the amount of free carboxylate surfactant, either because the calcium clays were reacting to consume sodium hydroxide or because they were reacting to precipitate calcium carboxylate. A reduction in the amount of carboxylate surfactant would be expected to increase primary recovery because a reduction should bring the concentration (which is too high) closer to the critical concentration. Various quantities of the clays were tested and primary recovery was found to increase as the amount of clay was increased. A maximum in primary recovery was eventually reached that then declined with a further increase in the amount of added clay. The produced water from the experiments which gave maximum primary recovery, 8.0 g in the calcium illite case and 10.0 g in the calcium illite case, was analyzed for ionic species and the data obtained served to confirm the predicted action of the clays. Recovery and froth quality data are recorded below in Table 6.13.

**Table 6.13.**

Additive			Primary froth			Secondary froth		
	1°R	2°R	%O	%w	%s	%O	%w	%s
None	49	47	70	25	6	61	26	12
Ca illite	89	8	75	17	8	41	42	17
Ca kaolinite	81	15	76	17	7	47	36	17

Calcium illite increased primary recovery to 89% while calcium kaolinite increased primary recovery to 81%. Both of the calcium clays increased the bitumen content of the primary froth at the expense of water.

Predictions can be made for the calcium clay systems based on reactions 6.1 through 6.3 given in the Introduction. The calcium clays would be expected to react with NaOH according to reaction 6.2 to yield sodium clays and precipitated calcium hydroxide (or carbonate). There are no ionic products from this reaction so that the only change expected in the ionic species analysis would be a disappearance of ionic species. Reaction 6.2 would be expected to be favoured at the expense of reaction 6.1 so a small decrease in the amount of bicarbonate would

be expected. Analyses were carried out for ionic species with the anionic species reported in Table 6.14.

**Table 6.14.** *Quantity of anionic species produced (meq/kg oil sand)*

NaOH	Ca added meq/kg	$\text{CO}_3^{2-}$	$\text{HCO}_3^-$	$\text{SO}_4^{2-}$	$\text{Cl}^-$	$\text{RCOO}^-$	Total
None		0.06	3.26	0.78	0.72	0.44	5.26
Ca illite	2.18	0.04	3.08	0.80	0.72	0.24	4.90
Ca kaolinite	0.90	0.02	3.12	0.54	0.70	0.24	4.62

Both calcium illite and calcium kaolinite acted to reduce the amount of free carboxylate surfactant from 0.44 meq surfactant/kg of oil sand to 0.24 meq/kg, which corresponds to the critical concentration. The increase in primary recovery noted above is due to this change. The initial low recovery is due to a carboxylate surfactant concentration that is too high while the high recoveries when clay was used were due to the reduction in surfactant concentration to near the critical concentration

In the calcium illite case the possible production of anionic species was 7.44 meq/kg (total of reference case plus amount added as calcium clay), while the actual amount produced was 4.90 meq/kg. As predicted (equation 6.2) there was a disappearance of anionic species. The same was true in the calcium kaolinite case. The possible production was 6.16 meq/kg while the actual production was 4.62 meq/kg.

There was also, as predicted, a small reduction in the amount of bicarbonate produced when calcium illite and calcium kaolinite were added. The reduction was only in the range of 0.4 to 0.6 meq bicarbonate/kg of oil sand but should be well within the accuracy and detection limit of the bicarbonate analytical method.

The cationic species analysis results are given in Table 6.15.

**Table 6.15.** *Quantity of cations produced (meq/kg oil sand)*

Additive	Ca <sup>2+</sup> added meq/kg	Na <sup>+</sup>	Fe <sup>2+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	K <sup>+</sup>	Total
None		6.24	0	0	0	0	6.24
Ca illite	1.09	10.02	0	0	0	0	10.02
Ca kaolinite	0.45	4.38	0	0	0	0	4.38

In all cases the only cation present in the produced water was sodium, which is in agreement with expectation. The amount of cationic species produced was in agreement with the amount of anionic species produced except in the calcium illite case. Here the amount of cationics exceeded the amount of anionics, probably as a result of an error in the determination of sodium.

The results described above are in agreement with the initial hypothesis that the calcium clays would act either to consume sodium hydroxide and thus reduce the amount of sodium hydroxide available for production of carboxylate surfactants or to precipitate insoluble calcium carboxylate surfactants or both.

## CONCLUSIONS

The data presented in this chapter support the proposal that some oil sands contain divalent carbonates, sulfates, and clays and that these materials act either to consume sodium hydroxide, making it unavailable for the production of carboxylate surfactants, or to consume carboxylate surfactant directly by precipitation as divalent metal salts, or both.

## REFERENCES

- Baptista, M. V. Role of the exchangeable cations of oil sand clays in oil sand processing – Part 1. Batch tests, AOSTRA J. Research (1989) 5, 237–241.
- Ferris, A.P., and Jepson, W.B. The exchange capacities of kaolinite and the preparation of homoionic clays, J. Colloid and Interface Science (1975) 51 245–259.



- Holm, L.W., and Robertson, S.D. Improved micellar/polymer flooding with high-pH chemicals, *J. Pet. Technol.* (1981) 33, 161–172.
- Kotlyar, L.S., Sparks, B.D., and Kodama, H. Some chemical and mineralogical properties of fine solids derived from oil sand, *AOSTRA J. Res.* (1984) 1, 99–106.
- Mikula, R.J., Munoz, V.A., and Lam, W. W. Correlations between oil sands minerals and processing characteristics, *J. Can. Pet. Technol.* (1989) 28 29–32.
- Mohnot, S.M., and Bae, J.H. A study of mineral/alkali reactions – Part 2, *SPE Reservoir Engineering* (1989) 4, 381–390
- Schramm, L.L. Ph.D. Thesis, Dalhousie University, Halifax, Nova Scotia (1980) 239 pp.

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***Alternatives to the Direct Use of  
Sodium Hydroxide as a Process Aid***



## INTRODUCTION

The results reported in Chapters 5 and 6 suggest the possible use of commercial surfactants to improve operation of the process. A process based on commercial surfactants would be of comparable cost to the current sodium hydroxide based process if operation could be achieved at or near the critical concentration, as measured by Schramm and Smith. Such a process could even show improved economics over the sodium hydroxide process for low grade oil sands because, as shown in Chapter 6, much of the sodium hydroxide added to low grade oil sands is consumed by reaction with divalent clays and other minerals. If a commercial surfactant could be found that would not undergo side reactions with divalent compounds, then optimization of the process using commercial surfactants at the Schramm/Smith critical concentration would be less expensive than using sodium hydroxide.

Some experimental work has been carried out (Sanford and Seyer, 1979) with commercial surfactants, including a commercial detergent (Tide), sodium oleate, and sodium lignosulfonate from the pulp and paper industry. It was found that these surfactants were able to optimize primary recovery from the hot water process, but not at the concentrations called for by Schramm and Smith. In the sodium oleate case it was found that a quantity of the material equivalent to 0.10 wt.% of the oil sand was required to increase primary recovery the same amount as was achievable with sodium hydroxide. Since this amounts to a concentration of about 2.20 meq/L it is much too high to be economic. In commercial practice about 2 kg of sodium oleate would be required to process 2000 kg of oil sand to produce about 1 barrel of bitumen. At a cost of, say, \$1.00 per kg for the oleate the cost would be on the order of \$2.00 per barrel of bitumen, which compares unfavorably with a cost of about \$0.10 per barrel of bitumen for sodium hydroxide.

The possibility exists that the natural surfactants involved in the hot water process are better at promoting the process than the commercial surfactants tested by Sanford and Seyer. The work of Dobrogowska and Hepler, referred to previously (Chapters 3 and 4), indicates that the natural surfactants may be obtainable for use in the process by alkaline air oxidation of bitumen. A brief investigation of the alkaline air oxidation of bitumen to produce carboxylates and the use of these carboxylates as additives for the hot water process has been carried out by Smith and Hepler. This research is described in this chapter.



## **EXPERIMENTAL**

### **Air Oxidation of Bitumen**

The bitumen sample, naphtha (if used), water, and sodium hydroxide were weighed into a 1 litre 3 necked round bottom flask fitted with a magnetic stirrer, an air sparger, and a condenser. The bitumen used in the experiments was commercial bitumen prepared by the hot water flotation process.

Air sparging was begun and the contents of the flask were brought to reflux and maintained at reflux for the specified time. The reaction mixture was allowed to cool to room temperature and decanted, filtered and ultrafiltered. The ultrafiltered product was then analyzed for basic species concentrations and the material was also used as an additive for batch extractions as described below.

### **Oil Sand**

The oil sand (20 kg) used in the experiments was obtained, as freshly mined material, from the Syncrude mine site at Mildred Lake. The oil sand was homogenized by chopping to a uniform small size using the edge of a 9 inch spatula and by mixing the chopped material in a large plastic bag. The homogenized oil sand was stored in a freezer at  $-30^{\circ}\text{C}$  with samples removed as required. The oil sand was found to contain 8.89% bitumen, 4.89% water, 86.2% solids and 25.8% of fine material (less than  $44\text{ }\mu\text{m}$  size).

### **Batch Extractions**

The procedure described in Appendix 3 was used. Some experiments were carried out using sodium hydroxide and some experiments were carried out using partially oxidized bitumen as process aid.

### **Basic Species Concentrations**

The concentration of unreacted sodium hydroxide in the air oxidation reaction mixtures was determined by titration of the ultrafiltered reaction mixture with

standard (0.006 N) hydrochloric acid. The titration end point was determined from the first derivative of the titration curve.

The concentration of total carboxylate in the air oxidation reaction mixtures was determined by first adjusting the pH of the ultrafiltered reaction mixture to 3 with dilute hydrochloric acid, degassing the acidified sample by sparging the solution with nitrogen and readjusting the solution pH to about 8 with dilute sodium hydroxide solution. The treated solution was then titrated with standard (0.006 N) hydrochloric acid and the end point (at about pH 5.3) was determined from the first derivative of the titration curve.

## **RESULTS AND DISCUSSION**

The procedure described in the experimental section was used to produce oxidation product by air oxidation of bitumen. Three oxidations were carried out with the experimental conditions given in Table 1.

**Table 7.1. Oxidation reaction conditions**

Expt. no.	Bitumen (g)	Naphtha (g)	H <sub>2</sub> O (mL)	NaOH mL, 1N	Time at reflux (hr)	NaOH (g)
SH 1	1.0	1.0	400	100	2.5	4.0
SH 2	1.0	1.0	500	0	2.5	0
SH 3	4.0	0	450	50	5.0	2.0

The first experiment (SH 1) used bitumen, naphtha and sodium hydroxide and was heated at reflux for 2.5 hours. The second experiment (SH 2) used bitumen and naphtha but was carried out without sodium hydroxide. It was also refluxed for 2.5 hours. The third experiment (SH 3) used bitumen and sodium hydroxide but was carried out without naphtha. It was heated at reflux for 5 hours.

The oxidation reaction mixtures were ultrafiltered and analyzed for hydroxide and total carboxylate by the procedure given in the experimental section.

Before carrying out batch extraction experiments to test the oxidation reaction mixtures for their effect on the hot water process, it was necessary to first process

samples of an oil sand at standard conditions using sodium hydroxide. The data from these experiments are given in Table 2.

*Table 7.2. Batch extraction experiments with sodium hydroxide*

Expt. no.	NaOH added (wt%)	Primary recovery (%)	Secondary recovery (%)	Total recovery (%)
89-22	0.00	65	21	86
89-23	0.03	69	17	86
89-24	0.05	76	9	84
89-25	0.07	79	6	85
89-33	0.07	77	7	84
89-26	0.09	76	8	83
89-34	0.09	80	3	83
89-27	0.12	63	20	83

The oil sand gave a primary recovery of about 60% when it was processed without sodium hydroxide and required about 0.07 wt% sodium hydroxide to yield maximum primary recovery which was about 78%.

The first oxidation reaction mixture (SH-1) had hydroxide concentration of about 180 meq/L of unreacted hydroxide (3.60 g of the 4.0 g used in the experiment) and a total carboxylate concentration of 0.44 meq/L (which amounts to about 130 mg/L if it is assumed that the molecular weight of the produced carboxylate is about 300 g/mol). The procedure was judged successful in that carboxylate species were produced from the bitumen. The conversion of bitumen to carboxylate was, however, very low and most of the sodium hydroxide remained unreacted.

According to the Schramm/Smith results, a carboxylate surfactant concentration of 0.12 meq/L (at the flooded tailings stage) is required to optimize primary recovery from the process. This concentration, when back-calculated to the slurry stage of the process (using the water quantities given in the procedure in Appendix 3) becomes about 0.84 meq/L. This concentration is not achievable with the first oxidation reaction product, because the total carboxylate concentration of 0.44 meq/L is too low. There would be required something like 290 mL of the

oxidation product to achieve the desired carboxylate surfactant concentration at the slurry stage while the procedure calls for a maximum of 150 mL of slurry water. Not only is it impossible to achieve the desired carboxylate surfactant concentration with the first oxidation product, it is also apparent that even the maximum usable amount of the product (150 mL) would supply enough sodium hydroxide to optimize the process and the use of 290 mL would provide an overdose of sodium hydroxide. Consequently, the first oxidation product was judged to be a poor source of carboxylate surfactant for the hot water process and no batch extraction experiments were carried out.

The second oxidation reaction was carried out without the addition of sodium hydroxide in an attempt to produce a solution of carboxylate free of sodium hydroxide. The experiment produced a solution that contained very little carboxylate and it was concluded that successful oxidation of bitumen requires at least some hydroxide. Again no batch extraction experiments were carried out.

The third oxidation experiment was carried out with an increased amount of bitumen, a decreased amount of sodium hydroxide, and a longer reaction time was used. The reaction product was found to contain about 78 meq/L of unreacted hydroxide (1.6 g unreacted out of 2.0 g used) and about 3.0 meq/L of carboxylate. There was still a considerable quantity of unreacted sodium hydroxide but there was an improvement in the amount of produced carboxylate over the first experiment. If the assumption is made that all the produced carboxylate is surface active, then about 45 mL of the reaction product, used as part of the slurry water, should result in a carboxylate concentration of 0.84 meq/L at the slurry stage. This calculation assumes, of course, that the sodium hydroxide in the reaction mixture will not interfere by producing more carboxylate surfactant. If the assumption is made that only the sodium hydroxide in the reaction mixture will act to optimize the process, then the quantity of reaction mixture required to optimize primary recovery is about 100 mL because this quantity of reaction mixture, if used at the slurry stage, is expected to produce a sodium hydroxide concentration of 0.07 wt%. Since it is expected that both the carboxylate and the sodium hydroxide will be active, and, since it is expected that not all of the carboxylate will be surface active, it becomes impossible to predict how much of the oxidation reaction mixture will be required to optimize recovery. However, if the carboxylate in the mixture does act to optimize the hot water process, then the quantity of reaction mixture needed for maximum



primary recovery should be less than 100 mL. If the carboxylate in the mixture does not act to optimize the process, then it would be expected that maximum primary recovery would occur at 100 mL.

The third oxidation reaction mixture was tested at three concentrations using the Syncrude batch extractor with the test mixture added at the slurry stage. The experimental data are given in Table 3.

**Table 7.3. Batch extraction experiments with SH-3 mixture**

Expt. no.	SH-3 added (mL)	Primary recovery (%)	Secondary recovery (%)	Total recovery (%)
89-203	25	65	20	85
89-204	50	73	13	86
89-205	100	72	8	81

The data are plotted in Figure 7-1, along with the data for processing the study oil sand with sodium hydroxide. There is no discernable difference between the points for sodium hydroxide and the points for the SH 3 oxidation reaction mixture when the points for the oxidation mixture are plotted as a function of the sodium hydroxide that the mixture brings to the batch extraction experiment. It can be concluded that the carboxylate in the third oxidation reaction mixture does not act to optimize primary recovery from the hot water process.

More research is needed into the use of commercial surfactants as an alternative to the use of sodium hydroxide. The search should be directed towards finding a commercial surfactant that will promote primary recovery at or near the concentration measured by Schramm and Smith for the natural surfactants, bearing in mind that it will be necessary to look at surfactants that are not consumed by the divalent materials present in oil sands.

## REFERENCES

Sanford, E. C., and Seyer, F. A. "Processibility of Athabasca tar sand using a batch extraction unit: the role of NaOH," CIM Bulletin (1079) 72, 164-169.

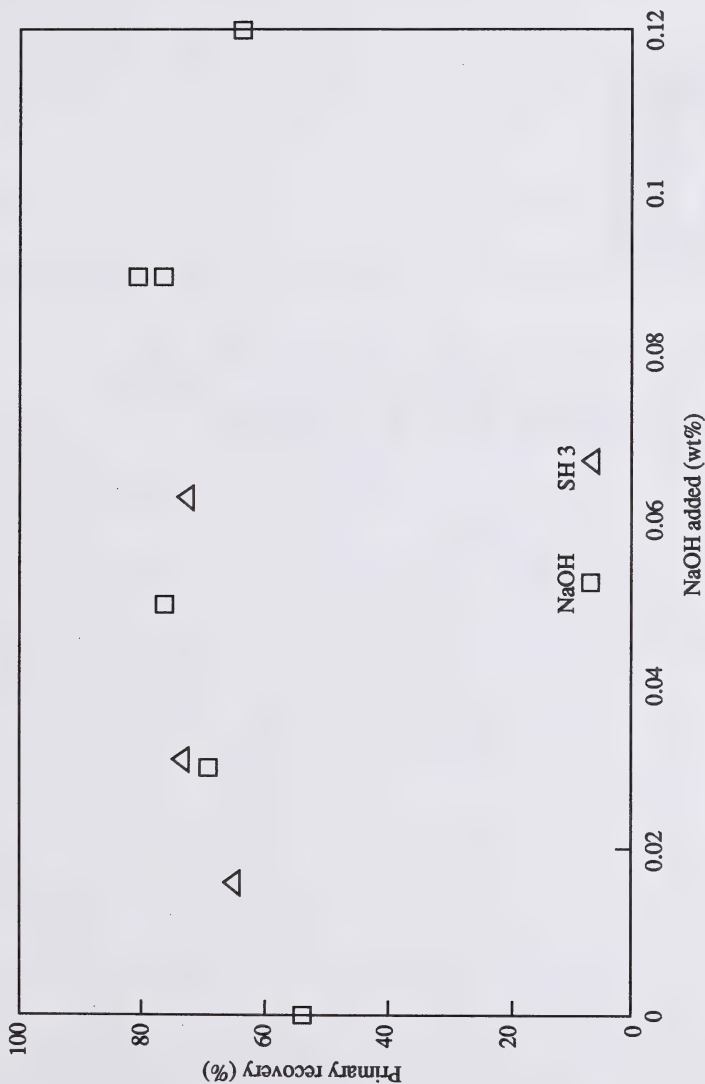


Figure 7.1. Primary recovery with NaOH and SH 3.



# 8

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## *Some Considerations for Further Research and Development*





## **INTRODUCTION**

The ideas and suggestions that are presented in this chapter are based on the following:

- (i) Results of previous research by ourselves;
- (ii) Results of previous research by others at Syncrude;
- (iii) Results of previous research at the Alberta Research Council;
- (iv) Results of previous research carried out in several universities, with support from AOSTRA;
- (v) Published results of other research done in various universities, in governmental research laboratories, and in industry;
- (vi) Operating experience at Syncrude;
- (vii) Many useful discussions, especially with colleagues at Syncrude and AOSTRA.

Some of the ideas and suggestions that are presented in this chapter are truly our own, some have come directly from our colleagues at Syncrude and AOSTRA, and some are hard-to-trace descendants of discussions with colleagues at Syncrude, AOSTRA, and elsewhere.

Although we have tried to avoid wild "shot in the dark" suggestions, we have consciously chosen to be bold rather than cautious in our selection of ideas and suggestions to present in this chapter.

Much of our focus throughout this book has been on the separation of bitumen from mined oil sands, largely because this was the focus of the AOSTRA-sponsored research that provided the initial motivation for writing this book. But it is well known at Syncrude (and throughout the industry) and at AOSTRA that separating bitumen from mined oil sands must be considered in relation to the *whole* process, which includes mining, transport of mined oil sands, possible effects due to storage, supply of water and chemicals for separation, tailings storage and treatment, upgrading and related need for hydrogen, problems with gaseous pollutants, storage or use of coke, etc. Each of these considerations involves scientific principles,

engineering practicalities, capital equipment costs, operating costs, and risks of expensive failures.

As specific examples of the many relationships between different parts of the whole process of mining, separation of bitumen, and upgrading, we mention that modifications in the hot water separation process can lead to important changes in the amount and properties of tailings and can have an effect on upgrading because of the increasing or decreasing amount of solids and water in the separated bitumen. As also discussed later, replacing the hot water separation process by some substantially different process (cold water, solvent extraction, direct coking) can also affect both tailings and upgrading.

To provide some perspective on the economic importance of the separation part of the total process of producing synthetic crude from mined oil sands, we mention that operating costs at Syncrude for the three principal processes that we label mining, separation, and upgrading are in the approximate ratio of 4:1:4; capital costs are distributed in about the same proportions.

Because the separation step is the least expensive of the three principal steps in producing synthetic crude from mined oil sands, it follows that a very large (say about 50%) reduction in cost of separation leads to a relatively small (about 5%) reduction in total cost. Balancing the clear gain from such a hypothetical lowering of cost of separation against the possibility of an expensive failure (or even a long delay in achieving efficient production) might very well lead to the sensible decision to continue with the present process.

Although considerations expressed in the preceding paragraph are certainly important, especially with respect to possible large changes in the hot water separation process or adoption of a substantially different process, there remain attractive possibilities for improvements of two kinds. (i) Relatively small changes in the hot water process might have important advantages, as discussed later in this chapter. (ii) True alternatives to the hot water separation process are possible (probably unlikely) for Syncrude (and Suncor), but could be very attractive for any new operation leading to production of synthetic crude from mined oil sands.

Relatively small changes (with correspondingly small costs and risks) in the present hot water process can have effects that are cumulatively large. The costs of

mining oil sands and moving the mined oil sands from the pit to the separation plant are independent of the percentage recovery of bitumen. Increasing the percentage recovery therefore leads to an effective decrease in mining cost per unit of produced synthetic crude. If such improved recovery also leads to higher quality separated bitumen (better quality froth in the separation step), there will be lower costs associated with upgrading. Finally, it is also possible that small changes in the hot water process can lead to a lesser (or larger) problem with tailings.

We turn now from generalities to some specifics.

## **POSSIBLE IMPROVEMENTS IN THE HOT WATER PROCESS**

Reasonable possibilities for improvements in the presently used hot water process include modifications that might lead to higher yields from high fines ores, from aged ores, or from other ores presently yielding less than the usual good recovery. In addition to the possibility of improving recovery from certain kinds of ores, there are good chances for improvements in treatment of froth, leading to bitumen that will contain lower than present amounts of solids and water that add to the difficulty and expense of upgrading.

Some general background related to the possibilities mentioned above is provided by Bichard's account (1987) of his research on oil sands for Imperial Oil during the period 1957–1965. Further background is provided by Camp (1976), by Erskine (1984), and in other references that have been cited (especially in Chapter 2) in this book.

It has been known since the early work of K. A. Clark that there is a general correlation of percentage recovery (also called processibility or processability) of bitumen with the amount of "fines" (mostly clays) in the mined ore to be treated by the hot water process. In general, recovery of bitumen decreases as the fines content increases. Early (still useful) accounts of the role of fine minerals in the hot water process have been provided by Clark and Pasternack (1932 and 1949).

More recently, Sanford (1983) has summarized many experimental results that lead to two important general conclusions. First, he has shown that increasing fines content leads to a requirement for increasing amounts of sodium hydroxide to



obtain maximum recovery of bitumen. Second, he has shown that maximum recovery usually decreases as content of fines in the ore increases.

In this same paper Sanford (1983) described his theory or model of processibility that provides useful partial explanations for this general trend of decreasing recovery with increasing content of fines; his theory also addressed other factors such as the role of process aids (especially NaOH) and mechanical energy input. Altogether, this work by Sanford and other research that he has cited has provided much of the background for the more recent research described in this book in Chapters 4–7.

Although the general trend of decreasing recovery of bitumen with increasing content of fines in the ore to be processed is well established, there are important exceptions.

Some of the exceptions to the generality that recovery of bitumen decreases with increasing content of fines in the ore have been cited by Smith, Ehrlich, and Hardin (1985), Axelson et al. (1989), Baptista (1989, two papers), and Mikula et al. (1989). We call particular attention to the work by Baptista (1989), who has investigated the effects of polyvalent metal ions on recovery of bitumen.

A principal aim of the AOSTRA-sponsored research at Syncrude and the Alberta Research Council that forms the basis for Chapters 4–7 in this book was to gain improved understanding of the reasons for the requirement for increased amounts of sodium hydroxide and decreasing recovery as fines content increases.

Some of the apparently erratic dependence of recovery on fines content can be attributed to using an amount of sodium hydroxide that leads to production of either too much or too little surfactant to be in accord with the “critical concentration” of free surfactant postulated by Schramm and Smith; see Chapter 3 for references to their research and a summary of evidence for this critical concentration. Here we emphasize that it is the concentration of *free* surfactant that is important; surfactant that is adsorbed on fine minerals or precipitated by reaction with polyvalent ions is not “free” to function in the separation process. This concept of a critical concentration of *free* surfactant is supported by results of research on Utah tar sands by Misra et al. (1981) and by Hupka and Miller (1991).

Achieving the desired critical concentration of free surfactant is done by adding the appropriate amount of sodium hydroxide. Some of the recent research at Syncrude was directed at obtaining understanding of why the amount of sodium hydroxide needed to reach maximum recovery varies from one ore to another. Results of this research have been reported in Chapters 5 and 6.

The research described in Chapters 5 and 6, supplemented by earlier results cited in Chapters 2-4, leads to the following conclusions. The amount of sodium hydroxide to be added to obtain the critical concentration of free surfactant and thence the maximum recovery of bitumen depends on the fines content, on the amounts of polyvalent ions, and on the acidity or basicity of the ore to which the sodium hydroxide is to be added. Partial explanations for these general correlations are as follows.

The observation that the amount of sodium hydroxide required to reach maximum recovery increases with increasing content of fines can be understood on the basis that some of the surfactant produced by reaction of sodium hydroxide with polar constituents of bitumen is adsorbed by the fines and is thence unavailable for participation in the separation process. It is therefore necessary to compensate for this adsorption of surfactant by adding more sodium hydroxide, which leads to production of enough "extra" surfactant to reach the critical concentration of *free* surfactant.

Some of the recent research at Syncrude by Smith (see Chapter 6) focussed on the role of polyvalent metal ions in the separation process and the requirement for increased sodium hydroxide that is associated with high fines ores. It has been known for a long time that anionic surfactants (such as in ordinary soap) are precipitated by reaction with polyvalent metal ions in hard water. Similarly, the surfactants produced by reaction of polar components of bitumen with sodium hydroxide can be precipitated by reaction with polyvalent metal ions, which leads to a requirement for more hydroxide to produce more surfactant and thence produce the desired critical concentration of free surfactant.

Smith's research has shown that these polyvalent metal ions also react directly with hydroxide ion to precipitate the corresponding metal hydroxides. These precipitation reactions that remove hydroxide ions from solution thus lead to a requirement for more added hydroxide to react with bitumen and thence produce the desired critical concentration of free surfactant.

Here we note that there is a general correlation of amounts of polyvalent metal ions with fines content. Since increasing fines content and increasing amounts of polyvalent metal ions are both associated with a need for increased amounts of sodium hydroxide to reach maximum recovery of bitumen, we have a good explanation for the general correlation that high fines ores require large amounts of sodium hydroxide to reach maximum recovery, as shown by Sanford (1983).

Smith's research on polyvalent metal ions also provides an explanation for some of the exceptions to the general (but not universal) correlation of fines content with amount of sodium hydroxide required to reach maximum recovery, as noted by several investigators cited earlier. For many ores for which there is a good correlation between fines content and polyvalent metal ion content, the amount of sodium hydroxide required to reach maximum recovery correlates well with either fines content or with polyvalent metal ion content. It is for historical reasons that this useful correlation is made in terms of fines content rather in terms of polyvalent metal ion content. On the other hand, there are other ores for which there is a poor correlation of fines content with polyvalent metal ion content. But for these ores there is usually a correlation of processibility (recovery) with amount of sodium hydroxide used and with polyvalent metal ion content, as noted by Baptista (1989). An explanation for this latter correlation is provided by the results obtained by Smith, as reported in Chapter 6 and discussed in preceding paragraphs.

The early work of Schramm and Smith showed that it takes several experiments to pinpoint the amount of added sodium hydroxide that leads to maximum recovery from any particular ore. Applying this kind of multi-experiment procedure has been very useful in connection with improving our understanding of the hot water process, but is a practical way to decide on the best amount of sodium hydroxide to add on an industrial scale only when very similar ores are to be processed for a relatively long time. Knowledge of the kinds that have been reported in this book, supplemented by results of various kinds of on-line analysis of ore, can be used to choose close to the optimum dosage of sodium hydroxide when the properties of the ore vary from "normal".

We now turn to consideration of the observed decrease in maximum recovery that is associated with increasing fines content in the ore; this decrease in maximum recovery occurs even when the optimum amount of sodium hydroxide is used as



process aid. The research of Schramm (1989) at Syncrude and of Takamura and Wallace (1988) and Chow (1991) at the Alberta Research Council provides some understanding of this problem, along with information that is significant with respect to the quality of froth. Some of Tyerman's research at Syncrude that is described in Chapter 4 is also relevant to this problem of froth quality.

As background for discussion of the research cited in the preceding paragraph, we mention that the part of the separation process under consideration here involves the flotation of aerated bitumen that occurs in the primary and secondary flotation vessels. In each case, relatively dense minerals are settling to the bottom while the aerated bitumen is floating toward the top to form the froth that is ultimately recovered. In general, the course sand settles as desired, but there are complications associated with the desired flotation of bitumen and the related settling of fine minerals. Some of the fine minerals that are supposed to settle float to the top (froth) with the bitumen; some of the bitumen that is supposed to float to the top settles with the fine minerals. The first problem leads to low quality froth, while the second leads to decreased recovery of bitumen. In addition to the problems with quality of froth and loss of bitumen to tailings, the suspension of bitumen and fines in the middle part of the flotation vessel can have such high viscosity that both flotation and settling become very slow.

Fine minerals that float to the top of the separation vessel with the aerated bitumen lead to what is described as lower quality froth and thence to bitumen containing suspended or trapped minerals, which are troublesome in the following upgrading. In addition to this problem of poor froth quality associated with floating minerals, Schramm's (1989) research demonstrated that the suspended fine minerals lead to increased viscosity and thence to the decreased rates of flotation of bitumen and settling of minerals as mentioned above.

The related research of Takamura and Wallace (1988) and Chow (1989) provides further information about the role of fines in flotation. An important distinction between what they call stable (more often called dispersed) suspensions and coagulated suspensions follows from their results. According to their work (see Figure 5 in the paper by Takamura and Wallace and Figure 4.20 in this book, Chapter 4), the operating conditions (minimal addition of sodium hydroxide, low concentration of sodium ions in process water) leading to maximum recovery from

high grade (low fines) ores correspond to “stable” or dispersed suspensions of clays; the flotation process works best when the concentration of suspended fines is reasonably low and when these fines are in a dispersed state. On the other hand, the operating conditions (addition of large amounts of sodium hydroxide) associated with processing lower grade (higher fines) ores correspond to coagulated suspensions of fine minerals (clays). Thus, it appears that the decreased recovery of bitumen from high fines ores (or other ores requiring addition of larger than usual amounts of sodium hydroxide) can be attributed to the effects of coagulated clays in the flotation vessels.

All of these results together lead us to suggest that it might be beneficial to use a combination of sodium hydroxide and an anionic surfactant as process aids for high fines ores.

It may be that considerations similar to those summarized above are pertinent to the problem of inclusion of large amounts of solids in the froth that is produced in the Sury (1990) process that was discussed in Chapter 2 and that is discussed further in the next section of this chapter.

Long ago Bichard (published in 1987) noted that samples of oil sand that were exposed to air (oxygen) were generally more acidic than were samples that had not been exposed to air. He attributed this acidity to oxidation of sulfide minerals and was able to correlate ore acidity with amount of sulfate (produced by oxidation of sulfide). More recently, Schramm and Smith (1987, two papers) have carried out systematic investigations of processibility of aged oil sands, with results that supplement in useful ways those reported earlier by Bichard. The results of Schramm and Smith also point toward oxidation of sulfide minerals (especially pyrite,  $\text{FeS}_2$ ) as a principal contributor to what is called “aging” and the related decrease in processibility. They have emphasized that ions of iron ( $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ ) in water can affect the concentration of free surfactant by reaction (precipitation) with hydroxide to decrease the amount of hydroxide that is available to react with bitumen and thence produce surfactant. In addition, these polyvalent ions react with surfactant after it is produced to form a precipitate, which decreases the concentration of free surfactant. Extraction tests in which a chelating agent (EDTA) was added showed that complexing polyvalent ions to minimize reaction with hydroxide and with produced surfactant substantially reversed the effects of aging.



Still more recently, Wallace, Henry, and Takamura (1989) have also concluded that oxidation of sulfide minerals is responsible for decreased processibility due to aging. They have focussed on the effects of increased ionic strength (more dissolved ions) in process water on froth quality, and have shown that their "ionizable surface group" model and related theory leads to the prediction that aged oil sands yield sufficiently high ionic strengths to cause coagulation of fine particles and thence also leads to deterioration in froth quality.

Investigations cited in the preceding two paragraphs have attributed difficulties in processing aged ores to oxidation of sulfides, leading to lower pH (increased acidity), increase in concentration of polyvalent ions and consequent effects on concentration of free surfactant, and to coagulation of fines and thence to deterioration of froth quality. Research by Dobrogowska and Hepler (summarized in Chapter 4) showed that mild oxidation of bitumen by the oxygen in air can lead to substantial changes in the bitumen-water interfacial tension, which in turn may have substantial effects on the separation process and on properties of froth.

Now, to conclude this part of Chapter 8, we mention some ideas that might be pursued to improve processibility of "problem ores" (due to aging, high fines content, etc.) or to improve the quality of froth.

- (i) We suggest that it might be possible to use inexpensive surfactants in the tumbler to saturate some of the fine minerals so that they will not adsorb the "active" surfactants produced by reaction of sodium hydroxide with acidic components of bitumen. This use of added surfactant might also directly aid the separation step and thence be a total or partial substitute for sodium hydroxide as a process aid. This use of surfactants as a process aid is most likely to be beneficial in connection with processing relatively low grade (high fines) or aged (oxidized) ores.
- (ii) We suggest that froth, probably after dilution, might be slightly acidified and/or treated with calcium ( $\text{Ca}^{2+}$ ) ions to promote coagulation of fine minerals, and thence lead to decreased mineral content in the separated bitumen.
- (iii) Theoretical and practical work by Masliyah at Syncrude and at the University of Alberta and by others at Syncrude has provided evidence that multi-stage

inclined plate settlers can work well and can be less expensive than centrifuges for froth treatment. This approach deserves further consideration.

- (iv) An alternative to froth treatment with centrifuges or inclined plate settlers has been proposed in connection with plans for the OSLO plant for extracting bitumen from mined oil sands. This proposed alternative involves heating the diluted froth to some high temperature (such as 250°C). Details of the proposed process have not been published in the open literature, nor do we have specific information about the quality (water and mineral content) of the bitumen that is obtained in this way. In spite of this lack of specific information, the possibility of a froth treatment process that does not involve either centrifuges or inclined plate settlers is attractive. We therefore recommend that heating processes receive further consideration.

We also remind the reader that Tyerman's extensive research on properties of froth (partly summarized in Chapter 4) provides much useful background and information.

## **ALTERNATIVES TO THE HOT WATER PROCESS**

Several alternatives to the hot water process have been described in Chapter 2. Here we offer some opinions about potential advantages of these alternative processes.

One of the most attractive of these alternative processes is the cold water process that has been described in Sury's patent (1990). It appears that this process is likely to be less expensive than the conventional hot water process and that the "fines problem" in tailings is reduced as compared with the tailings from the hot water process. The principal identifiable problem with the Sury process is that the froth contains more solids than does the froth obtained with the usual hot water process. Improvements in froth treatment that are desired in connection with improving the conventional hot water process may be even more important in connection with the Sury process. It may be that the OSLO proposal to heat diluted froth to a high temperature will lead to the desired reduction in amount of solids in produced bitumen.

It has been known for a long time that ultrasonic agitation of a suspension of oil sands in water can lead to separation and recovery of the bitumen. It has also been known for a long time (for example, Bichard, 1957–1965, published in 1987) that such reagents as sodium silicate and sodium phosphate (instead of sodium hydroxide) can be used as process aids for the separation of bitumen from mined oil sands. Recently, a low temperature process involving both sonication and use of the process aids mentioned above has been described in a series of journal articles and patents by Sadeghi et al. (1988–1992). We summarize this process as follows.

Mined oil sands are mixed with water containing an alkaline process aid (sodium silicate, sodium phosphate, sodium carbonate) and agitated with ultrasonics (sometimes also with mechanical shear). In addition to an alkaline process aid, low concentrations of free radical initiators (such as benzoyl peroxide or hydrogen peroxide) have been used to reduce the time required for good recovery of bitumen. Some of the experimental results that have been reported show that process water containing surfactants produced by the combination of sonication and reaction of bitumen with process aids can be used several times; this repeated use reduces the effective cost of the chemical process aids. It is also claimed that the process leads to precipitation of asphaltene and “preasphaltene” as solids, which means that the recovered deasphalted bitumen has higher API gravity than did the original bitumen and can be described as partly upgraded. There has also been discussion of separation of potentially valuable minerals; this subject has been discussed earlier in this book.

It is our opinion that there are many questions still to be answered about the process described by Sadeghi et al. (1988–1992). Some of these questions are related to real difficulties associated with processing very large amounts of mined oil sand in short times and then carrying out the appropriate separations of partly upgraded bitumen and the solid asphaltene plus preasphaltene, while others are related to the economics of ultrasonic agitation (expensive as compared with either direct thermal energy or mechanical energy applied to the tumbler) and cost of process aids. Still other questions arise in connection with potential problems that might be associated with variations in ore quality, properties of tailings, amount of process water needed, etc.

Along with consideration of questions mentioned above, the Sadeghi process deserves further consideration because of the possibility that their partially upgraded (deasphalted) bitumen might be further upgraded and refined in easier and less



expensive ways than are presently used for whole bitumen. At present, there is some disagreement among those who work with upgrading in industry and university research laboratories as to the amount of saving that might be achieved by starting with deasphalted bitumen. It is, however, generally agreed that an upgrading process for deasphalted bitumen must be accompanied by some other process that makes use of the separated asphaltenes. If one or more uses for asphaltenes can be found and it is also found that there are economic advantages to be associated with upgrading and refining deasphalted bitumen, it will also be necessary to consider conventional deasphalting of bitumen obtained by the presently used hot water process (or the Stry cold water process).

Because substantial fractions of the total costs of the processes now used at Syncrude and Suncor are associated with upgrading, the possibility of using a separation process that yields partially upgraded bitumen deserves serious consideration. In this connection, we mention that one of the advantages of various direct heating/coking/distillation processes such as proposed by Peterson and Gischler (1951) and more recently by Taciuk (1984) is that the bitumen is partly upgraded during the process.

Since one of the attractive features of thermal processes mentioned in the sentence above is the absence of wet tailings, it is now appropriate to turn to the question of dealing with the wet tailings that are an almost inevitable product of any hot or cold water separation process. At present, the produced tailings are stored in large ponds; some of the water is recycled, but the total amount of tailings is increasing. Properties of tailings and many proposed treatments of tailings have been described in a review by Kasperski (1992).

Some of the recent public discussion of tailings has been oriented toward total elimination of tailings ponds associated with the hot water process, and probably to be associated with any other water-based process. Such complete elimination of tailings ponds requires that tailings be processed continuously as they are produced. Since any continuous process is subject to occasional decreased throughputs or even complete breakdowns, total elimination of tailings ponds would mean that throughput of the separation process would have to be correlated closely with the tailings treatment process, including unscheduled slowdowns or shutdowns. Because of such difficulties, we suggest that it makes much better sense to permit the continued use of



approximately steady-state tailings ponds of strictly limited size. If this suggestion is accepted, it will be absolutely necessary to treat tailings at a long term average rate that is approximately the same as the rate of production of tailings, but the short term correlation of production rate with treatment rate would not be required.

In spite of recent advances that have been made in methods of treating wet tailings, it may be that the cost of such treatment makes non-water processes more attractive. The absence of a need for treatment of wet tailings combined with the possibility of reduced costs for upgrading might make various (dry) high temperature processes or various solvent extraction processes economically and environmentally attractive.

We have already mentioned the Peterson-Gischler and Taciuk thermal processes for treating mined oil sands. Now we remind readers of the sand reduction process (described in Chapter 2) that was developed by Bichard et al. (1963), and also described in Bichard's book (1987). This combination of sand reduction followed by high temperature treatment of sand-depleted ore might be advantageous, as originally noted in the publications cited above.

Several solvent extraction processes and related (water plus solvent) processes have been described in Chapter 2. Each of these processes has potential advantages that have been noted by the developers, and each has the disadvantage of using some solvent that is more valuable than the bitumen that is produced, which means that very efficient recovery of solvent is necessary. This requirement for recovery of solvent is not necessarily insurmountable; consider that a diluent is used in treatment of the froth from the conventional hot water separation process and that an acceptable fraction of this diluent is recovered for further use.

## **CONCLUDING COMMENTS AND RECOMMENDATIONS**

Although the principal focus in this book has been on processes for separating bitumen from mined oil sands, we have discussed the potential (not yet established) advantages of a process that leads to deasphalted bitumen. In order to assess the possible reality of such advantages, it will be necessary to conduct some investigations on upgrading deasphalted bitumen.

In addition, it will be necessary to investigate possible uses of the asphaltenes that are not upgraded. Burning these asphaltenes for fuel is possible, but is almost certainly beset with difficulties similar to those associated with burning coke. Sadeghi et al. (1988–1992) have suggested that the asphaltene and preasphaltene that are separated from bitumen in their process might serve as useful feedstock for unspecified chemical production processes; some research in this area might be rewarding. Is it possible that some as yet undeveloped chemical treatment of asphaltenes could lead to inexpensive surfactants to be used in the separation process, as discussed earlier in this chapter?

In this chapter and in earlier chapters we have cited publications in which various theories or models of the separation hot water process are presented. Although there are uncertainties and a few controversies about specifics, it is our opinion that these presentations constitute a generally accurate and useful picture of the first part of the hot water separation process. But these publications are mostly less concerned with and hence less useful with respect to aeration of bitumen and the processes taking place in the flotation vessels. We suggest that more attention, both experimental and theoretical, should be devoted to the interaction of air bubbles with bitumen and with fine minerals, to the properties of aqueous suspensions of bitumen (emulsions) that also contain fine minerals, and to the properties of froth.

## REFERENCES

- Axelson, D.E., Mikula, R.J., and Potoczny, Z.M. Characterization of oil sands mineral components and clay-organic complexes, *Fuel Sci. & Technol. International* (1989) 7, 659–673.
- Baptista, M.V. Role of the exchangeable cations of oil sand clays in oil sand processing — Part 1. Batch tests, *AOSTRA J. Research* (1989) 5, 237–241.
- Baptista, M.V. Role of the exchangeable cations and iron-amorphous coatings of the oil sand solids in oil sand processing — Part 2. Pilot and plant tests, *AOSTRA J. Research* (1989) 5, 243–256.

- Bichard, J.A. *Oil sands composition and behavior research; the research papers of John A. Bichard. 1957–1965*, (1987) Alberta Oil Sands Technology and Research Authority, Edmonton.
- Bichard, J.A. Bowman, C.W., Butler, R.M., and Tiedje, J.L., Separation of oil from the Athabasca oil sands by sand reduction, in *The K.A. Clark volume*, (1963) ed. M.A. Carrigy, Information Series No. 45, Research Council of Alberta, Edmonton.
- Camp, F.W. *The tar sands of Alberta, Canada*, 3rd ed., (1976) Cameron Engineers, Inc. Denver.
- Chow, R.S. The stability of kaolinite-in-water dispersions, *Colloids and Surfaces* (1991) 61, 241–253.
- Clark, K.A., and Pasternack, D.S. Hot water separation of bitumen from Alberta bituminous sand, *Ind. Eng. Chem.* (1932) 24, 1410–1416.
- Clark, K.A., and Pasternack, D.S. The role of very fine mineral matter in the hot water separation process as applied to Athabasca bituminous sand, Research Council of Alberta (1949), Report No. 53.
- Erskine, H.L. Suncor hot water process, Chapter 5.1 in *Handbook of synfuels technology*, ed. R.A. Meyers (1984), McGraw-Hill, New York.
- Hupka, J., and Miller, J.D. Electrophoretic characterization and processing of Asphalt Ridge and Sunnyside tar sands, *Int. J. Mineral Processing* (1991) 31, 217–231.
- Kasperski, K. A review of properties and treatment of oil sands tailings, *AOSTRA J. Research* (1992) 8, 11–53.
- Mikula, R.J., Munoz, V.A., and Lam, W.W. Correlations between oil sands minerals and processing characteristics, *J. Can. Petrol. Technol.* (1989, November–December) 29–32.
- Misra, M., Aguilar, R., and Miller, J.D. Surface chemistry features in the hot water processing of Utah tar sand, *Separation Sci. and Technol.* (1981) 16, 1523–1544.

- Peterson, W.S., and Gischler, P.E. The fluidized solids technique applied to the Alberta oil sands problem, in *Proceedings: Athabasca oil sands conference*, (1951) Government of Alberta, pp. 207–236, Edmonton.
- Sadeghi, M-A., Sadeghi, K., Kuo, J-F., Jang, L-K., and Yen, T.F. Treatment of carbonaceous materials, U.S. Patent (1988) 4,765,885.
- Sadeghi, K.M., Sadeghi, M-A., and Yen, T.F. Novel extraction of tar sands by sonication with the aid of in situ surfactants, *Energy & Fuels* (1990) 4, 604–608.
- Sadeghi, M-A., Sadheghi, K., Kuo, J-F., Jang, L-K., and Yen, T.F. Treatment of carbonaceous material, U.S. Patent (1991) 5,017,281.
- Sadeghi, K.M., Sadeghi, M-A., Jang, L-K., Chilingarian, G.V., and Yen, T.F. A new bitumen recovery technology and its potential application to remediation of oil spills, *J. Petrol. Sci. & Eng.* (1992) 8, 105–117.
- Sadeghi, K.M., Sadeghi, M-A., Kuo, J-F., Jang, L-K., Lin, J-R., and Yen, T.F. A new process for tar sand recovery, *Chem. Eng. Comm.* (1992) 117, 191–203.
- Sanford, E.C. Processibility of Athabasca oil sand: Interrelationship between oil sand fine solids, process aids, mechanical energy and oil sand age after mining, *Can. J. Chem. Eng.* (1983) 61, 554–567.
- Schramm, L.L. The influence of suspension viscosity on bitumen rise velocity and potential recovery in the hot water flotation process for oil sands, *J. Can. Petrol. Technol.* (1989, May–June) 28, 73–80.
- Schramm, L.L., and Smith, R.G. Some observations on the aging phenomenon in the hot water processing of Athabasca oil sands. Part. 1. The nature of the phenomenon, *AOSTRA J. Research* (1987) 3, 195–214.
- Schramm, L.L., and Smith, R.G. Some observations on the aging phenomenon in the hot water processing of Athabasca oil sands. Part 2. The mechanism of aging, *AOSTRA J. Research* (1987) 3, 215–224.
- Smith, M.M., Ehrlich, R., and Hardin, A. A Study of Fourier grain shape analysis and batch recoveries of bitumen from Athabasca oil sands, *AOSTRA J. Research* (1985) 1, 245–253.



- Sury, K.N. Low temperature bitumen recovery process, (1990) U.S. Patent 4,946,597.
- Taciuk, W. Development status of the Taciuk direct thermal processor for oil sands and heavy oils, in *The future of heavy crude and tar sands*, 2nd International UNITAR Conference (1984), pp. 1096–1103, ed. R.F. Meyer, J.C. Wynn, and J.C. Olson, McGraw-Hill, New York.
- Takamura, K., and Wallace, D. The physical chemistry of the hot water process, J. Can. Petrol. Technol. (1988, November–December) 27, 98–106.
- Wallace, D., Henry, D., and Takamura, K. A physical chemical explanation for deterioration in the hot water processability of Athabasca oil sand due to aging, Fuel Sci. & Technol. International (1989) 7, 699–725.



# APPENDIX

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# 1

*Dimensions, Units, and  
Some Important Properties*





Dimensions of some quantities of interest to us can be expressed in terms of combinations of mass, length, time, and electric current:

- Energy (also work and heat):  $(\text{mass})(\text{length})^2(\text{time})^{-2}$
- Force:  $(\text{mass})(\text{length})(\text{time})^{-2}$
- Power:  $(\text{mass})(\text{length})^2(\text{time})^{-3}$
- Pressure:  $(\text{mass})(\text{length})^{-1}(\text{time})^{-2}$
- Area:  $(\text{length})^2$
- Volume:  $(\text{length})^3$
- Electric charge:  $(\text{current})(\text{time})$
- Electric potential:  $(\text{mass})(\text{length})^2(\text{time})^{-3}(\text{current})^{-1}$
- Electric resistance:  $(\text{mass})(\text{length})^2(\text{time})^{-3}(\text{current})^{-2}$
- Electric conductance:  $(\text{mass})^{-1}(\text{length})^{-2}(\text{time})^3(\text{current})^2$
- Electric capacitance:  $(\text{mass})^{-1}(\text{length})^{-2}(\text{time})^4(\text{current})^2$

The expressions above are consistent with the following:

$$\begin{aligned}\text{Energy} &= (\text{force})(\text{length}) = (\text{pressure})(\text{length})^3 = (\text{pressure})(\text{volume}) \\ &= (\text{elect. potential})^2(\text{time})(\text{elect. resistance})^{-1} \\ &= (\text{current})^2(\text{elect. resistance})(\text{time}) \\ &= (\text{elect. potential})(\text{elect. charge})\end{aligned}$$

$$\text{Power} = (\text{energy})(\text{time})^{-1} \text{ or } \text{Energy} = (\text{power})(\text{time})$$

$$\text{Pressure} = (\text{force})(\text{length})^{-2} = (\text{force})(\text{area})^{-1}$$

Surface (or interfacial) tension can be expressed in terms of force and length or energy and area as in the following:

$$\begin{aligned}\text{Surface (interfacial) tension} &= (\text{force})(\text{length})^{-1} \\ &= (\text{energy or work})(\text{area})^{-1}\end{aligned}$$

We also have

$$\begin{aligned}\text{Dynamic ("absolute") viscosity} &= (\text{mass})(\text{length})^{-1}(\text{time})^{-1} \\ &= (\text{energy})(\text{volume})^{-1}(\text{time}) \\ &= (\text{pressure})(\text{time})^{-1}\end{aligned}$$

The relationship between dynamic viscosity and kinematic viscosity is

$$\begin{aligned}\text{Kinematic viscosity} &= (\text{dynamic viscosity})(\text{density})^{-1} \\ &= (\text{length})^2(\text{time})^{-1}\end{aligned}$$

The expressions for dynamic and kinematic viscosities above lead to

$$\text{Energy} = (\text{dynamic viscosity})(\text{volume})(\text{time})^{-1}$$

and

$$\text{Energy} = (\text{kinematic viscosity})(\text{mass})(\text{time})^{-1}$$

There are many units that we might use for mass, length, time, electric current, energy, pressure, etc. In practice, however, we need consider only a few of the many possibilities. Results of many recent investigations have been reported in SI units, but results of some recent investigations have been reported in non-SI units and results of many earlier investigations were reported in terms of non-SI units. It is therefore useful to consider both SI and non-SI units as follows.

The new SI system is closely related to the older cgs (centimeter, gram, second) and mks (meter, kilogram, second) systems. In the cgs system, a fundamental unit of force was the dyne, with the corresponding unit of energy being the erg, which is equal to one dyne cm. In the SI system, a fundamental unit of force is the newton (equal to  $10^5$  dynes), with the corresponding unit of energy being the joule, which is equal to  $10^7$  ergs.

Some SI units and symbols, relationships (conversion factors) between various units and also values of certain constants are given in Table 1-A.

***Table 1-A. Units, symbols, and values of important quantities***

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Names and symbols for SI base units

Mass: kilogram, kg

Length: metre, m

Time: second, s

Electric current: ampere, A

Thermodynamic temperature: kelvin, K

*Table 1-A continued*

*Table 1-A continued ...*

Physical quantities, names of SI units, and symbols

Force: newton,  $N = \text{kg m s}^{-2}$

Pressure: pascal,  $\text{Pa} = \text{kg m}^{-1} \text{s}^{-2} = \text{N m}^{-2}$

Energy: joule,  $J = \text{kg m}^2 \text{s}^{-2}$

Power: watt,  $W = \text{kg m}^2 \text{s}^{-3} = \text{J s}^{-1}$

Electric charge: coulomb,  $C = \text{A s}$

Electric potential: volt,  $V = \text{kg m}^2 \text{s}^{-3} \text{A}^{-1} = \text{J A}^{-1} \text{s}^{-1}$

Electric resistance: ohm,  $\Omega = \text{kg m}^2 \text{s}^{-3} \text{A}^{-2} = \text{V A}^{-1}$

Electric conductance: siemens,  $S = \text{kg}^{-1} \text{m}^{-2} \text{s}^3 \text{A}^2 = \Omega^{-1}$

Electric capacitance: farad,  $F = \text{kg}^{-1} \text{m}^{-2} \text{s}^4 \text{A}^2 = \text{A s V}^{-1}$

Units of energy

1 joule (J) = 1 newton meter (N m) = 1 watt second (W s)  
 $= 10^7 \text{ ergs} = 10^7 \text{ dyne cm} = 1 \text{ volt coulomb (V C)}$   
 $= 9.48 \times 10^{-4} \text{ Btu}$

1 calorie (cal) = 4.184 J =  $3.97 \times 10^{-3} \text{ Btu}$

1 kcal = 4.184 kJ = 3.97 Btu

1 L atm = 101.33 J = 24.218 cal

1 kJ = 0.278 kW h

1 kW h = 3.600 kJ

Units of pressure

1 pascal (Pa) =  $10^{-5} \text{ bar} = 10 \text{ dyne cm}^{-2}$   
 $= 9.869 \times 10^{-6} \text{ atm} = 1.450 \times 10^{-4} \text{ psi}$

1 bar =  $10^5 \text{ Pa} = 0.9869 \text{ atm} = 750.06 \text{ torr (torr = mm Hg)}$

1 atm = 101325 Pa = 101.325 kPa = 760 torr

Units of volume

1  $\text{m}^3$  = 1000 L = 35.3 cubic ft = 8.39 barrel (US petroleum)  
 $= 264 \text{ US gallons}$

1 barrel (US petroleum) = 159 L = 0.159  $\text{m}^3$   
 $= 34.97 \text{ Imperial gallons}$   
 $= 42 \text{ US gallons}$

1 Imperial gallon = 4.549 L = 1.201 US gallon

*Table 1-A continued*

Table 1-A continued ...

Units of mass

$$1 \text{ kg} = 1000 \text{ g} = 2.205 \text{ lb}$$

$$1 \text{ ton} = 2000 \text{ lb} = 907.2 \text{ kg}$$

$$1 \text{ tonne} = 1000 \text{ kg} = 2205 \text{ lb} = 1.102 \text{ ton}$$

Units of energy/mass

$$1 \text{ Btu lb}^{-1} = 2.324 \text{ J g}^{-1} = 0.5554 \text{ cal g}^{-1}$$

Units of force

$$1 \text{ dyne (dyn)} = 1 \times 10^{-5} \text{ newton (N)} = 1 \text{ g cm s}^{-2}$$

$$1 \text{ newton (N)} = 1 \text{ kg m s}^{-2} = 10^5 \text{ dyne}$$

Units of surface tension

$$1 \text{ dyne cm}^{-1} = 1 \text{ erg cm}^{-2} = 10^{-3} \text{ newton meter}^{-1} \\ = 1 \text{ (mN m}^{-1}\text{)}$$

$$1 \text{ J m}^{-2} = 1 \text{ N m}^{-1} \text{ or } 1 \text{ (mJ m}^{-2}\text{)} = 1 \text{ (mN m}^{-1}\text{)}$$

Units of dynamic ("absolute") viscosity

$$1 \text{ poise (p)} = 1 \text{ dyn s cm}^{-2} = 10^{-5} \text{ N s cm}^{-2} = 0.1 \text{ Pa}\cdot\text{s}$$

$$1 \text{ cp} = 0.01 \text{ p} = 0.001 \text{ Pa}\cdot\text{s} = 1 \text{ mPa}\cdot\text{s}$$

Gas constant (R) =  $8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$

$$= 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$$

$$= 82.06 \text{ cm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$$

$$= 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$= 0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1}$$

Avogadro's constant ( $L$  or  $N_A$ ) =  $6.022 \times 10^{23} \text{ mol}^{-1}$

Boltzmann constant ( $k = R/L$ ) =  $1.3807 \times 10^{-23} \text{ J K}^{-1}$

Faraday constant (F) =  $96,485 \text{ C mol}^{-1}$

Permittivity of vacuum:  $8.854 \times 10^{-12} \text{ F m}^{-1}$

Ice point ( $0^\circ\text{C}$ ) =  $273.15 \text{ K}$

Triple point (ice, water, vapor) =  $273.16 \text{ K}$

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Numerical values (with units) of several properties of several substances are summarized in the following tables.



**Table 1-B. Specific heats of some minerals**

Mineral	$c_p / \text{J K}^{-1} \text{g}^{-1}$		
	300 K	400 K	500 K
SiO <sub>2</sub> (quartz)	0.743	0.889	0.990
CaCO <sub>3</sub> (calcite)	0.835	0.969	1.044
CaMgCO <sub>3</sub> (dolomite)	0.855	0.995	1.095
MgCO <sub>3</sub> (magnesite)	0.904	1.074	1.185
Kaolinite	0.962	1.151	1.270
Illite	0.808	0.955	1.046
Montmorillonite	0.811	0.996	1.084

These specific heats are from Hepler, L.G. Thermodynamic and thermochemical properties, Chapter 4 in *AOSTRA technical handbook on oil sands, bitumens and heavy oils*, (1989), ed. L.G. Hepler and C. Hsi, Alberta Oil Sands Technology and Research Authority, Edmonton.

Molar heat capacities of many minerals have been tabulated in an excellent book: Robie, R.A., Hemingway, B.S., and Fisher, J.R. *Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10<sup>5</sup> pascals) pressure and at higher temperatures*, Geological Survey Bulletin 1452, U.S. Government Printing Office, Washington, D.C. (1978). Reprinted with corrections (1979).

**Table 1-C. Equations to represent specific heats of minerals from the Athabasca deposit. Specific heats are expressed in terms of  $\text{J K}^{-1} \text{g}^{-1}$  and temperatures are kelvins (K)**

Athabasca coarse solids, mostly SiO<sub>2</sub>, >325 mesh:

$$c_p = 0.168 + 2.442 \times 10^{-3} T - 1.611 \times 10^{-6} T^2$$

$$c_p = 0.914 + 0.331 \times 10^{-3} T - 2.415 \times 10^{-4} T^{-2}$$

Athabasca fine solids, mostly clays, <325 mesh:

$$c_p = 0.342 + 1.873 \times 10^{-3} T - 0.926 \times 10^{-6} T^2$$

$$c_p = 0.787 + 0.644 \times 10^{-3} T - 1.559 \times 10^{-4} T^{-2}$$

All of these equations are taken from Cassis, R., Fuller, N., Hepler, L.G., McLean, R.J.C., Skauge, A., Srinivasan, N.S., and Yan, H-k., Specific heat capacities of bitumens and heavy oils, reservoir minerals, clays, dehydrated clays, asphaltenes and cokes, AOSTRA J. Research (1985) 1, 163–173. The equations for specific heats of coarse solids are for the temperature range 300–700 K while the equations for fine solids are for the temperature range 320–680 K. Equations expressed in terms of  $T^2$  are generally best for extrapolating to lower temperatures, while equations expressed in terms of  $T^{-2}$  are generally best for extrapolating to higher temperatures.

**Table 1-D. Heats of combustion**

Substance	Heat of combustion (exothermic)/kJ g <sup>-1</sup>
Anthracite	33–37
Bituminous coal	25–35
Sub-bituminous coal	18–28
Lignite	13–18
Charcoal	29
Gasoline	46–48
Kerosene	44–48
Bitumen from Athabasca	41.5
Syncrude gas oil	44.5
Syncrude synthetic crude	45.7
Syncrude naphtha	44.6–46.4
Syncrude H-oil pitch	38.6
Asphaltenes from Athabasca	36.9
Maltenes from Athabasca	42.2
Syncrude coke	28.9–29.7

These heats of combustion are taken from Hepler (as cited below Table 1-B).

**Table 1-E. Specific heats of bitumen and related substances from Athabasca. Specific heats are expressed in terms of  $J K^{-1} g^{-1}$  and temperatures are kelvins (K)**

Substance	Specific heat
Bitumen	$c_p = 0.055 + 6.818 \times 10^{-3} T - 4.464 \times 10^{-6} T^2$ $c_p = 1.763 + 1.542 \times 10^{-3} T - 4.884 \times 10^{-4} T^{-2}$
Asphaltenes	$c_p = -0.593 + 8.079 \times 10^{-3} T - 5.353 \times 10^{-6} T^2$ $c_p = 1.444 + 1.748 \times 10^{-3} T - 5.609 \times 10^{-4} T^{-2}$
Syncrude coke	$c_p = -0.141 + 3.928 \times 10^{-3} T - 2.108 \times 10^{-6} T^2$ $c_p = 0.778 + 1.239 \times 10^{-3} T - 2.739 \times 10^{-4} T^{-2}$

These equations are taken from Cassis et al. as cited following Table 1-C. The equations represent the specific heats of bitumen over the temperature range 300–600 K, of asphaltenes over the temperature range 280–620 K, and of coke over the temperature range 280–720 K. Equations expressed in terms of  $T^2$  are generally best for extrapolating to lower temperatures, while equations expressed in terms of  $T^{-2}$  are generally best for extrapolating to higher temperatures.

**Table 1-F. Some properties of water**

$t/^{\circ}C$	density/ $g\ cm^3$	surface tension /[(mN)/m]	viscosity/mPa·s
0	0.9998	75.6	1.787
20	0.9982	72.8	1.002
40	0.9922	69.6	0.653
60	0.9832	66.2	0.466
80	0.9718	62.6	0.355
100	0.9584	58.9	0.282

Surface tension expressed in terms of milli-newton/meter (mN/m) as above is numerically equal to the value expressed in terms of dyne/cm. Viscosity expressed in terms of milli-pascal second as above is numerically equal to the value expressed in terms of centipoise (cp).

t/°C	vapor pressure/mm Hg	vapor pressure/kPa	dielectric constant
0	4.6	0.61	87.9
20	17.5	2.33	80.2
40	55.4	7.38	73.2
60	149.4	19.9	66.7
80	355	47.4	60.9
100	760.0	101.3	55.5

Specific heats of ice and water and enthalpies of vaporization of water are as follows:

- $c_p$  (ice, 220–273 K,  $\text{J K}^{-1} \text{g}^{-1}$ ) =  $0.136 + 0.0072 T$
- $c_p$  (average for liquid water, 273–373 K) =  $4.2 \text{ J K}^{-1} \text{g}^{-1}$
- $\Delta H = 2500 \text{ J g}^{-1}$  at  $0^\circ\text{C}$
- $\Delta H = 2442 \text{ J g}^{-1}$  at  $25^\circ\text{C}$
- $\Delta H = 2257 \text{ J g}^{-1}$  at  $100^\circ\text{C}$

An authoritative source of accurate values of properties of water and steam is the following: Haar, L., Gallagher, J.S., and Kell, G.S. *NBS/NRC steam tables: thermodynamic and transport properties and computer programs for vapor and liquid states of water in SI units*, (1984) Hemisphere Publ. Corp, Washington., and McGraw-Hill International Publ. Co., Toronto.

**Table I-G. Some properties of Athabasca bitumen**

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Heat of combustion (constant volume, exothermic) =  $41.5 \text{ kJ g}^{-1}$

Specific heat/ $(\text{J K}^{-1} \text{g}^{-1}) = 0.055 + 6.818 \times 10^{-3} T - 4.464 \times 10^{-6} T^2$   
 $= 1.763 + 1.542 \times 10^{-3} T - 4.884 \times 10^{-4} T^{-2}$

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The equations above represent the experimental specific heats over the range 300–600 K. The equation expressed in terms of  $T^2$  is best for extrapolating to lower temperatures and the equation expressed in terms of  $T^{-2}$  is best for extrapolating to higher temperatures.

Viscosities of Athabasca bitumen that are calculated from the equation

$$\text{Viscosity}/(\text{mPa}\cdot\text{s}) = 4 \times 10^{-10} \exp(10100/T)$$

that was selected in Chapter 1 are as follows.

Temperature/°C	Viscosity/mPa
0	$5 \times 10^6$
10	$1 \times 10^6$
20	$4 \times 10^5$
30	$1 \times 10^5$
40	$4 \times 10^4$
50	$2 \times 10^4$
60	$6 \times 10^3$
70	$2 \times 10^3$
80	$1 \times 10^3$
90	$5 \times 10^2$
100	$2 \times 10^2$

Surface tensions (liquid-air interfacial tensions) of Athabasca bitumen have been reviewed in Chapter 1. For temperatures in the range 40 to 112°C, high and low values of values of surface tension of Athabasca bitumen range from 35 to 18 mJ m<sup>-2</sup> (or mN m<sup>-1</sup>). The surface tension of Athabasca bitumen decreases with increasing temperature at a rate of about 0.075 mJ m<sup>-2</sup> per °C.

***Table 1-H. Some properties of Syncrude naphtha***

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Density: 0.751 g cm<sup>-3</sup> at 20°C and 0.703 g cm<sup>-3</sup> at 80°C

Heat of combustion (constant volume, exothermic) = 44.6–46.4 kJ g<sup>-1</sup>

Viscosity/mPa·s =  $9.23 \times 10^{-3} \exp(1170/T)$

Boiling (atm pressure) range: 93–193°C

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The heat of combustion above is taken from Table 1-D. The equation for viscosity is from Schramm, L.L., and Kwak, J.C.T. The rheological properties of an Athabasca bitumen and some bituminous mixtures and dispersions, J. Can. Petrol. Technol. (1988, January–February) 27, 26–35.





# APPENDIX

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# 2

*Partial Characterization of Bitumen  
in Terms of Molecular Weights  
of Defined Components*



## INTRODUCTION

Truly detailed characterization of bitumen in terms of specific chemical compounds is impossible because of the large number of such compounds in any sample of bitumen. Further, such detailed molecular characterization is not directly related in any known way to properties such as viscosity and surface tension that are important in many industrial processes. On the other hand, it should be recognized that partial chemical characterization has been achieved in useful ways, as reviewed in a chapter by Strausz (1989). Such partial chemical characterization has occasionally focussed on identification and determination of molecular structures of specific compounds, but has more often focussed on defined classes of substances (sometimes called defined components) such as asphaltenes and maltenes.

In this appendix we present a review of efforts to characterize bitumen in terms of molecular weight and also in terms of the mass fractions and molecular weights of various defined fractions. This kind of characterization is truly necessary for a few purposes and may be useful for other purposes, as summarized below.

Solubilities of gases in bitumen can be expressed in any of several ways. One unambiguous kind of expression is in terms of mass percent of dissolved gas (at specified pressure and temperature), which does not require any knowledge of the molecular weight of bitumen. On the other hand, theoretically based efforts to use solubility data obtained at convenient temperatures and pressures in predicting solubilities at other pressures and temperatures require (Prausnitz et al., 1986; Bottomley et al., 1989) that solubilities be expressed in terms of mole fraction, which in turn requires knowledge of the average molecular weight of the bitumen. Lu and Fu (1989) have discussed some such correlations, with an emphasis on use of equations of state.

There are many correlations of properties such as vapour pressure (or related distillation characteristics) and viscosity with molecular weights of pure substances, and other correlations with mole fractions and molecular weights of components of mixtures. Such correlations can be useful in connection with the differences between properties of "native" bitumen and bitumen that has been diluted with naphtha or from which some or all of one defined component (such as the asphaltenes) has been removed.

Although this book is concerned primarily with the recovery of bitumen from mined oil sands, it is important to recognize that the separation process should be considered in relation to such matters as the amount and properties of tailings and that the properties of the recovered bitumen can be significant in connection with the subsequent upgrading process, as discussed in Chapter 8.

## **EXPERIMENTAL METHODS**

The classical methods for obtaining molecular weights of substances of low volatility (such as bitumen) are based on colligative properties of solutions, as explained in most textbooks of physical chemistry and also in a less mathematical book (Hepler and Smith, 1975). These colligative properties provide a measure of the numbers of "foreign" (from the point of view of the solvent) particles in dilute solutions. Colligative properties include the vapour pressure lowering and the freezing temperature lowering of a solvent due to presence of one or more dissolved substances. The general procedure involves preparing a solution that contains a known mass of some solvent (such as toluene) of already known molecular weight and a known mass of bitumen or other substance of as yet unknown molecular weight. Then the vapour pressure of the solvent in solution is measured and compared with the vapour pressure of the pure solvent at the same temperature, or the freezing temperature of the solution is measured and compared with the freezing point of the pure solvent. The resulting differences in vapour pressure ( $\Delta P$ ) or freezing temperature ( $\Delta T$ ) then lead to the desired average molecular weight of the bitumen or other substance that was dissolved in the solvent. Bulmer and Starr (1979), Wallace et al. (1988), and Wallace (1988) have provided specific discussions of applications of these methods to determination of the average molecular weight of bitumen. We also note that Chung et al. (1979) have provided a useful discussion of the application of vapour phase osmometry (most commonly used vapour pressure lowering method) to determination of average molecular weights of liquid fuels.

It is often useful to consider bitumen to be a mixture of "defined components," with each defined component present in some amount that can be measured. One common definition of components is based on solubility relationships; the "pentane insolubles" (usually called "asphaltenes") and the "pentane solubles" (usually called "maltenes") are in this case the defined



components. Other separation methods, such as gel permeation chromatography, lead to other defined components. All of these defined components are mixtures of more or less similar chemical substances; "similar" may refer to properties such as vapour pressure or boiling point, solubility in a specified solvent, chromatographic separation characteristics, etc.

Just as average molecular weights can be useful in helping to characterize whole bitumen, they can also be useful for characterizing defined components. Measurements of colligative properties such as vapour pressure lowering (usually by means of vapour pressure osmometry) and freezing point lowering are applicable to determination of the average molecular weights of defined components of bitumen. Speight et al. (1985) have provided a review of application of these and other methods to investigation of the molecular weights of asphaltenes.

Along with the recognized usefulness of average molecular weights, there have been questions at Syncrude Research, the Alberta Research Council, and elsewhere about the absolute accuracy and also the internal consistency of reported molecular weights of bitumen and defined components. Part of the purpose of this appendix is to provide examples (including results of unpublished research) of good and not-so-good internal consistency of average molecular weights and percent composition data. We also provide estimates of probable uncertainties, followed by brief mention of possible systematic errors and methods of minimizing these errors.

## **SOME MOLECULAR WEIGHTS OF WHOLE BITUMEN**

An extensive (not complete) summary of reported molecular weights of Athabasca bitumen is presented in Table 2-A. It should be recognized that these reported molecular weights refer to different samples of Athabasca bitumen. Some of these samples were coker feed bitumen from Syncrude or Suncor, while other samples were obtained by solvent extraction from mined oil sands. Some of the differences in reported molecular weights are due to "sample problems" such as presence of residual low molecular weight solvent or loss of light ends.

**Table 2-A. Some molecular weights of Athabasca bitumen**

Source	Molecular weight/g mol <sup>-1</sup>
Bowman (1967)	539
Berkowitz and Speight (1975)	540–800
Camp (1976)	539 and 600–700
Selucky et al. (1977)	540
Bunger et al. (1979)	568
Khan et al. (1984)	620
Mehrotra and Svrcek (1985)	595
Fu et al. (1985)	555
Lu et al. (1986)	544
Fu et al. (1986)	472–620
Chen et al. (1988)	560
Wallace (1988) and Wallace et al. (1988)	393–607
Mehrotra et al. (1988)	572
Strausz (1989)	490–620
Xu and Hepler (1990)	554
Wood and Hepler (unpublished)	566

## MOLECULAR WEIGHTS OF BITUMEN AND DEFINED COMPONENTS OF BITUMEN

Most methods for obtaining molecular weights lead to “number average” molecular weights. In the case of a pure substance, the number average molecular weight is also “the” molecular weight, but the situation is more complicated for mixtures.

As background for following calculations, we note that the units to be used for molecular weight are g mol<sup>-1</sup> and that the number of moles of substance in a given sample can be obtained as the mass of the sample divided by the molecular weight of the substance. Also, the molecular weight of a substance can be evaluated from the mass of a sample divided by the number of moles of the substance in the sample; this number of moles can be obtained from the results of measurements of a colligative property of a solution.

Because we are concerned here with the relationship between the average molecular weight of bitumen and the average molecular weights and mass percentages of various defined components, we begin by writing a general equation that relates these quantities:

$$(1) \quad 100/M = \Sigma(P_i/M_i) \text{ or } M = 100/\Sigma(P_i/M_i)$$

Here  $M$  represents the average molecular weight of a mixture of defined components, each  $M_i$  represents the average molecular weight of a defined component, and each  $P_i$  represents the mass percent of that defined component in the mixture.

For the specific case of bitumen that is considered to be a mixture of two defined components (asphaltenes and maltenes), equation (1) is written as

$$(2) \quad M_b = 100/[P_a/M_a] + (P_m/M_m)]$$

in which subscripts  $b$ ,  $a$ , and  $m$  indicate bitumen, asphaltenes, and maltenes, respectively.

Now we consider application of equation (2) to some experimental results and show how this kind of application can demonstrate that experimental results are or are not internally consistent.

As our first example, we consider results for Athabasca bitumen reported by Selucky et al. (1977) as follows:  $M_b = 540 \text{ g mol}^{-1}$ ,  $M_a = 4500 \text{ g mol}^{-1}$ ,  $P_a = 16.6$  mass percent,  $M_m = 435 \text{ g mol}^{-1}$ , and  $P_m = 83.4$  mass percent. All of these molecular weights were obtained by the usual method of vapour phase osmometry. We insert the above values of  $M_a$ ,  $P_a$ ,  $M_m$ , and  $P_m$  in equation (2) and calculate  $M_b = 512 \text{ g mol}^{-1}$ . This calculated  $M_b$  differs from the experimental value ( $540 \text{ g mol}^{-1}$ ) by 5%, which is consistent with reasonable estimates of uncertainties in the various experimental molecular weights and mass percentages of defined components present in the bitumen.

Selucky et al. (1978) have carried out similar investigations of bitumen from Cold Lake, leading to the following:  $M_b = 490 \text{ g mol}^{-1}$ ,  $M_a = 8,000 \text{ g mol}^{-1}$ ,  $M_m = 430 \text{ g mol}^{-1}$ ,  $P_a = 15.3$  mass percent, and  $P_m = 84$  mass percent. Using these latter

four values in equation (2) leads to a calculated  $M_b = 507 \text{ g mol}^{-1}$ . This calculated molecular weight of Cold Lake bitumen is in good agreement (3%) with the directly measured value, so again we have good internal consistency.

More recent investigations of Athabasca bitumen in the same laboratory (Chen et al., 1988 and 1989) have led to the following:  $M_b = 560 \text{ g mol}^{-1}$ ,  $M_a = 2,598 \text{ g mol}^{-1}$ ,  $M_m = 410 \text{ g mol}^{-1}$ ,  $P_a = 16.2 \text{ mass percent}$ , and  $P_m = 83.8 \text{ mass percent}$ . Using these latter four values in equation (2) leads to a calculated  $M_b = 475 \text{ g mol}^{-1}$ , which differs by 15% from the direct experimental value ( $560 \text{ g mol}^{-1}$ ). This difference between direct experimental molecular weight of whole bitumen and the value calculated from molecular weights and mass percentages of defined components shows that at least one of the reported quantities has an error that is larger than the uncertainties usually associated with these quantities. On the basis of comparison of the results cited above with those from several other investigations of Athabasca bitumen and its defined components, we suggest that the reported molecular weights of the defined components may be too small (for reasons discussed later in this appendix); combining more typical values of  $M_a = 5,000 \text{ g mol}^{-1}$  and  $M_m = 475 \text{ g mol}^{-1}$  with the reported values of  $P_a$  and  $P_m$  leads to a calculated  $M_b = 557 \text{ g mol}^{-1}$ , in excellent agreement with the directly measured value.

As another example, we consider the molecular weights and mass percent results for Athabasca bitumen from Wood and Hepler (unpublished) that were obtained by vapour phase osmometry and by measurements of freezing points of solutions made with benzene as solvent. Their results are as follows:  $M_b = 566 \text{ g mol}^{-1}$ ,  $M_a = 5057 \text{ g mol}^{-1}$ ,  $P_a = 15 \text{ mass percent}$ ,  $M_m = 517 \text{ g mol}^{-1}$ , and  $P_m = 85 \text{ mass percent}$ . Use of the values for  $M_a$ ,  $P_a$ ,  $M_m$ , and  $P_m$  in equation (2) leads to a calculated  $M_b = 597 \text{ g mol}^{-1}$ . The 5% difference between this calculated  $M_b$  and the direct experimental  $M_b = 566 \text{ g mol}^{-1}$  is consistent with reasonable estimates of uncertainties in the various experimental molecular weights and mass percent values.

Now consider some molecular weights and percent compositions for bitumen from Sunnyside, Utah, as reported by Bunker and Cogswell (1981). They characterized this bitumen as having  $P_a = 20.6 \text{ mass percent}$  and  $P_m = 79.4 \text{ mass percent}$ . Vapour phase osmometry, using benzene as solvent, led to the following molecular weights:  $M_b = 778 \text{ g mol}^{-1}$ ,  $M_a = 8,000 \text{ g mol}^{-1}$ , and  $M_m = 636 \text{ g mol}^{-1}$ . Using these latter two molecular weights and mass percentages of defined components



in equation (2) leads to a calculated  $M_b = 785 \text{ g mol}^{-1}$  for whole bitumen, which agrees remarkably well (within 1%) with the experimental value ( $778 \text{ g mol}^{-1}$ ).

Bunger and Cogswell (1981) have also applied vapour phase osmometry, using pyridine as solvent, to evaluation of molecular weights of the same bitumen and defined components discussed above, with the following results:  $M_b = 854 \text{ g mol}^{-1}$ ,  $M_a = 1160 \text{ g mol}^{-1}$ , and  $M_m = 615 \text{ g mol}^{-1}$ . Using these molecular weights for asphaltenes and maltenes and the corresponding mass percentages in equation (2) leads to a calculated  $M_b = 681 \text{ g mol}^{-1}$ . This calculated molecular weight for whole bitumen differs considerably (20%) from the corresponding experimental value. Good internal consistency of molecular weights and mass percentages does not prove that the experimental results are correct, but this poor internal consistency does demonstrate that at least one of the reported results contains a substantial error.

Champagne, Manolakis, and Ternan (1985) have used gel permeation chromatography to separate Athabasca bitumen into 11 fractions and have used several methods to obtain molecular weights of each fraction. Some similar results from the same laboratory were reported earlier by Furimsky and Champagne (1982). Using various combinations of the reported molecular weights and mass percentages of the 11 fractions, it is possible to calculate molecular weights of the original bitumen that range from  $559 \text{ g mol}^{-1}$  to  $669 \text{ g mol}^{-1}$ , with an average value about  $610 \text{ g mol}^{-1}$ . Neither set of investigators reported a directly determined average molecular weight of their sample of Athabasca bitumen, but we note that most of the recent results from other laboratories (see Table 2-A) are consistent with  $M_b \approx 565 \text{ g mol}^{-1}$ , which is in very good agreement with the smallest calculated value, differs from the average calculated value by 8%, and differs from the largest calculated value by 18%. All of these considerations lead us to suggest that the smallest molecular weights (determined by gas chromatography and mass spectroscopy) for the light fractions are probably more reliable than the larger values obtained in other ways.

Many researchers have carried out a wide variety of investigations intended to lead toward improved characterization of the asphaltenes fractions of bitumens, heavy oils, coal liquids, etc. Several of these investigations have focussed on separation of asphaltenes into several "components" that are defined in terms of solubilities, chromatographic separations, etc. Further investigations of these defined components have included measurements of average molecular weights as well as



other research that is indicated by the titles of some papers cited below. Here we will review results of some of these investigations, as reported by Strausz et al.

Ignasiak, Kemp-Jones, and Strausz (1977) separated asphaltenes from Athabasca bitumen and then applied vapour phase osmometry to determination of the average molecular weight. Their reported average molecular weights for whole asphaltenes, as determined using four different solvents, ranged from 5450 to 5920 g mol<sup>-1</sup>, with the average value being 5580 g mol<sup>-1</sup> (standard deviation = 223 g mol<sup>-1</sup>, which is 4% of the average molecular weight). These researchers extracted the asphaltenes with four polar solvents to obtain four defined components or fractions of the original asphaltenes and then made measurements leading to the average molecular weights of these fractions. Ignasiak et al. have applied their version of equation (1) to the mass percentages and molecular weights of the four fractions to obtain 3809 and 4891 g mol<sup>-1</sup> as calculated average molecular weights of whole asphaltenes; our calculations with the same results lead to 3896 and 4751 g mol<sup>-1</sup> for these average molecular weights. Differences between these calculated molecular weights and the directly measured values for whole asphaltenes range from 17 to 34%; these large differences show that there must be at least one error that is larger than the usual estimated uncertainties in molecular weights and mass percentages.

Ignasiak, Strausz, and Montgomery (1977) have also separated the asphaltenes from Athabasca bitumen and then separated the asphaltenes into four defined components. Their published results include the average molecular weights of the original asphaltenes and each of the four separated components, along with mass percentages of each component in the original whole asphaltenes. We use their reported molecular weights and mass percentages of components in equation (1) to obtain 4912 g mol<sup>-1</sup> as a calculated molecular weight for the original asphaltenes. This calculated molecular weight differs by 17% from the directly measured value (5900 or 5920 g mol<sup>-1</sup>), which again suggests the presence of at least one error that is larger than the usual estimates.

Because of the well-documented difficulties in determining molecular weights of asphaltenes (see the review by Speight et al., 1985) and other difficulties associated with chemical separations and subsequent determination of mass percentages and molecular weights of defined components, the discrepancies noted in the two preceding paragraphs were not entirely unexpected. Now it is encouraging to

note that results from a more recent investigation in the same laboratory show much better internal consistency and are probably more accurate, as summarized below.

Ignasiak et al. (1983) have reported on separation of the asphaltenes (average molecular weight =  $3600 \text{ g mol}^{-1}$ ) from Athabasca bitumen, followed by further separation of the asphaltenes into five fractions by gel permeation chromatography and then determination of mass percentages and molecular weights of each fraction. These authors have applied their version of equation (1) to the mass percentages and molecular weights of the five fractions to obtain  $3800 \text{ g mol}^{-1}$  for the average molecular weight of the original asphaltenes, which differs by only 6% from the directly measured  $3600 \text{ g mol}^{-1}$ . This discrepancy of 6% is consistent with usual estimates of uncertainties in molecular weights and compositions expressed in terms of mass percent.

As our last example of considerations of molecular weights and mass percentages of defined fractions or components, we consider the work of Kyriacou et al. (1988) on Cold Lake vacuum bottoms; this work was intended to provide a useful (in connection with upgrading and refining processes) correlation between molecular weights and viscosities. In one series of measurements these workers used vapour phase osmometry to obtain  $1400 \text{ g mol}^{-1}$  for the average molecular weight of their sample of Cold Lake vacuum bottoms. They also used gel permeation chromatography to separate the vacuum bottoms into nine fractions and then used vapour phase osmometry to obtain the molecular weights of the nine fractions. We have inserted their molecular weights and mass percentages of the nine fractions in equation (2) to calculate  $871 \text{ g mol}^{-1}$  for the average molecular weight of the original vacuum bottoms. This calculated molecular weight differs by 38% from the directly measured  $1400 \text{ g mol}^{-1}$ ; this large difference clearly indicates the presence of at least one substantial error in the reported results.

Kyriacou et al. (1988) have also applied field ionization mass spectroscopy to determination of the molecular weights of the Cold Lake vacuum bottoms and the nine separated fractions. In this way they obtained  $902 \text{ g mol}^{-1}$  for the average molecular weight of the original vacuum bottoms. Our use of their mass percentages and the corresponding molecular weights of the nine fractions obtained by way of mass spectroscopy leads us to a calculated  $930 \text{ g mol}^{-1}$  for the original vacuum bottoms, which is in good agreement (only 3% difference) with the corresponding value obtained by direct measurement.

We conclude from the results summarized above that the molecular weights obtained from mass spectroscopy are (in this case) more reliable than those from vapour phase osmometry.

Finally, we give one illustration of the application of a consistency test to the average molecular weights of "pseudo components" that are sometimes used in connection with phase equilibria. Mehrotra et al. (1985) have listed mass percentages and molecular weights of five pseudo components of Athabasca bitumen that they have used in connection with their calculations of phase equilibria. We have used their mass percentages and molecular weights in equation (2) to obtain a calculated value of  $M_b = 492 \text{ g mol}^{-1}$ , which is 10–20% too small in relation to the "best" values in Table 2-A.

## SENSITIVITY ANALYSIS

To begin our considerations of the effects of retention of solvent used for extraction or the effects of missing components due to vapourization of light ends or failure to remove polar substances from minerals, we describe an imaginary bitumen that is perfectly characterized as follows:  $P_a = 17.0$  mass percent asphaltenes of molecular weight  $M_a = 5000 \text{ g mol}^{-1}$  and  $P_m = 83.0$  mass percent maltenes of molecular weight  $M_m = 475 \text{ g mol}^{-1}$ . The average molecular weight of this imaginary whole bitumen is  $M_b = 561 \text{ g mol}^{-1}$ .

Now suppose that we have 100 g of this perfectly characterized bitumen that is contaminated by 2 g of toluene (molecular weight =  $92 \text{ g mol}^{-1}$ ). An accurate measurement of the average molecular weight of this mixture of bitumen and toluene by the freezing point method (using benzene as solvent) would lead to

$$M_b = 102/[17/5000] + (83/475) + (2/92)] = 510 \text{ g mol}^{-1}$$

This value differs from the "true" value by 9%.

Suppose that we had used benzene, instead of toluene, as the extracting solvent and that our working sample of supposedly pure bitumen was contaminated with 2% of benzene. An accurate measurement of the freezing point depression



(using benzene as the solvent) now leads to an error of only 2% in the calculated molecular weight.

Results of the calculations reported above show that it is best to use the same low molecular weight (volatile, removable by vapourization) solvent for extraction as will later be used as solvent in the freezing point experiment. Since it is more convenient to use benzene than it is to use toluene as solvent in applying the freezing point method of molecular weight determination, it is better to use benzene than toluene as extracting solvent.

Similar calculations (with similar results) can be carried out to assess the consequences of *non-volatile* contaminants on molecular weights of bitumen that are obtained from results of measurements using vapour phase osmometry or other measurements of vapour pressures. Assessments of errors associated with the presence of volatile contaminants are more complicated, requiring further information about the kind of measurement and also information about the vapour pressure of the contaminant. In general, however, it can be stated that it is best to use the same substance (often benzene or toluene) for extraction that will later be used as solvent for vapour phase osmometry, etc.

It is well known (for example, see Speight et al., 1985) that widely different values of molecular weights have been reported for asphaltenes from similar samples of bitumen. Part of the reason for this wide range can be understood in terms of the following calculations.

Suppose that we have a sample of asphaltenes for which the true molecular weight is  $5000 \text{ g mol}^{-1}$  and that this sample is contaminated (1%) with pentane. Freezing point depression measurements lead to a calculated  $M = 2968 \text{ g mol}^{-1}$ , which is in error by 41%. Because pentane is very volatile in the usual temperature range for vapour pressure measurements, this contaminant is likely to lead to a very large error in the molecular weight derived from such measurements.

Suppose that we have a sample of asphaltenes for which the "true" molecular weight is  $5000 \text{ g mol}^{-1}$ . Further suppose that a 100 g sample of asphaltenes is contaminated by 1.0 g of adsorbed or occluded light ends having average molecular weight equal to  $100 \text{ g mol}^{-1}$ . The derived molecular weight of this contaminated sample will then be

$$M_a = 101/[(100/5000) + (1/100)] = 3367 \text{ g mol}^{-1}$$

This value differs from the "true" value by 33%.

Similar calculations can be carried out to obtain estimates of the effect of residual solvent (such as pentane) on the molecular weight of maltenes as obtained from results of measurements of freezing point depression. As mentioned previously, there may be large effects due to *volatile* contaminants (such as pentane) on molecular weights obtained by way of vapour pressure measurements.

## REFERENCES

- Berkowitz, N., and Speight, J.G. The oil sands of Alberta, *Fuel* (1975) 54, 138–149.
- Bottomley, G.A., Smith, J.F., Schutte, R.P., and Hepler, L.G. Partial molar volumes and solubilities of gases in bitumen. *AOSTRA J. Research* (1989) 5, 383–390.
- Bowman, C.W. Molecular and interfacial properties of Athabasca tar sands, *Proceedings, 7th World Petroleum Congress* (1967), 3, 583–603.
- Bulmer, J.T., and Starr, J. ed., *Syncrude analytical methods for oil sand and bitumen processing*, (1979) Syncrude Canada Ltd, Edmonton.
- Bunger, J.W., Thomas, K.P., and Dorrence, S.M. Compound types and properties of Utah and Athabasca tar sand bitumens, *Fuel* (1979) 58, 183–195.
- Bunger, J.W., and Cogswell, D.E. Characteristics of tar sand bitumen asphaltenes as studied by conversion of bitumen by hydropyrolysis, Chapter 13 in *Chemistry of asphaltenes*, ed. J.W. Bunger and N.C. Li, *Advances in Chemistry Series* 195 (1981), American Chemical Society, Washington, D.C., pp 219–236.
- Camp, F.W. *The tar sands of Alberta, Canada*, 3rd ed., (1976), Cameron Engineers, Inc., Denver.
- Champagne, P.J., Manolakis, E., and Ternan, M. Molecular weight distribution of Athabasca bitumen, *Fuel* (1985) 64, 423–425.



- Chen, H.H., Montgomery, D.S., and Strausz, O.P. Hydrocracking of Athabasca bitumen using oil-soluble organometallic catalysts. Part I: The influence of temperature and pressure on catalytic activity, AOSTRA J. Research (1988) 4, 45-57.
- Chen, H.H., Montgomery, D.S., Strausz, O.P., and George, Z.M. Hydrocracking of Athabasca bitumen using oil-soluble organometallic catalysts. Part III: Optimization of liquid-phase hydrocracking conditions for mixtures of nickel and molybdenum naphthenates and coking studies on the hydrocracked product, AOSTRA J. Research (1989) 5, 33-48.
- Chung, K.E., Anderson, L.L., and Wiser, W.H. New procedure for molecular-weight determination by vapour-phase osmometry, Fuel (1979) 58, 847-852.
- Fu, C.-T., Puttagunta, R., and Vilcsak, G. Vapour-liquid equilibrium properties for pseudo-binary mixtures of CO<sub>2</sub>-Athabasca bitumen and N<sub>2</sub>-Athabasca bitumen, AOSTRA J. Research (1985) 2, 73-81.
- Fu, C.-T., Puttagunta, R., Baumber, L., and Hsi, C. Pseudo-critical properties of heavy oils and bitumens, Fluid Phase Equil. (1986) 30, 281-295.
- Furimsky, E., and Champagne, P. J. Characterization of Athabasca bitumen fractions derived by gel permeation chromatography, Fuel Proc. Technol. (1982) 6, 269-275.
- Hepler, L.G., and Smith, W.L. *Principles of chemistry*, (1975) Macmillan, New York.
- Ignasiak, T., Kemp-Jones, A.V., and Strausz, O.P. The molecular structure of Athabasca asphaltene. Cleavage of the carbon-sulfur bonds by radical ion electron transfer reactions, J. Org. Chem. (1977) 42, 312-320.
- Ignasiak, T., Strausz, O.P., and Montgomery, D.S. Oxygen distribution and hydrogen bonding in Athabasca asphaltene, Fuel (1977) 56, 359-365.
- Ignasiak, T., Kotlyar, L., Samman, N., Montgomery, D.S., and Strausz, O.P. Preparative gel permeation chromatography of Athabasca asphaltene and the relative polymer-forming propensity of the fractions, Fuel (1983) 62, 363-369. The same molecular weights and mass percentages have been reported by Cyr, N., McIntyre, D.D., Toth, G., and Strausz, O.P. Hydrocarbon structural group analysis of Athabasca asphaltenes and its g.p.c. fractions by <sup>13</sup>C n.m.r., Fuel (1987) 66, 1709-1714.

- Khan, M.A.B., Mehrotra, A.K., and Svrcek, W.Y. Viscosity models for gas-free Athabasca bitumen. *J. Can. Petrol. Technol* (1984, May-June) 23, 47-53.
- Kyriacou, K.C., Baltus, R.E., and Rahimi, P. Characterization of oil residual fractions using intrinsic viscosity measurements, *Fuel* (1988) 67, 109-113.
- Lu, B.C.-Y., Chung, W.K., Adachi, Y., and Boublik, T. Correlation and prediction of solubilities of gases in Athabasca bitumen, *AOSTRA J. Research* (1986) 2, 139-146.
- Lu, B.C.-Y., and Fu, C.-T. Phase equilibria and PVT properties, Chapter 6 in *AOSTRA technical handbook on oil sands, bitumens and heavy oils*, (1989) ed. L.G. Hepler and C. Hsi, Alberta Oil Sands Technology and Research Authority, Edmonton,
- Mehrotra, A.K., and Svrcek, W.Y. Viscosity, density and gas solubility data for oil sands bitumen. Part I: Athabasca bitumen saturated with CO and C<sub>2</sub>H<sub>6</sub>, *AOSTRA J. Research* (1985) 1, 263-268.
- Mehrotra, A.K., Sarkar, M., and Svrcek, W.Y. Bitumen density and gas solubility predictions using the Peng-Robinson equation of state, *AOSTRA J. Research* (1985) 1, 215-229.
- Mehrotra, A.K., Svrcek, W.Y., Fu, C.-T., and Puttagunta, V. R. Reconciliation of gas-solubility data, *AOSTRA J. Research* (1988) 4, 237-243.
- Prausnitz, J.M., Lichtenthaler, R.N., and Gomes de Azevedo, E. *Molecular thermodynamics of fluid phase equilibria*, 2nd ed. (1986) Prentice-Hall, Inc. Englewood Cliffs, New Jersey.
- Selucky, M.L., Chu, Y., Ruo, T., and Strausz, O.P. Chemical composition of Athabasca bitumen, *Fuel* (1977) 56, 369-381.
- Selucky, M.L., Chu, Y., Ruo, T.C., and Strausz, O.P. Chemical composition of Cold Lake bitumen, *Fuel* (1978) 57, 9-16.

Speight, J.G., Wernick, D.L., Gould, K.A., Overfield, R.E., Rao, B.M.L., and Savage, D.W. Molecular weight and association of asphaltenes: a critical review, *Rev. Inst. Français du Petrol.* (1985, No. 1) 40, 51–61.

Strausz, O. P. Bitumen and heavy oil chemistry, Chapter 3 in *AOSTRA technical handbook on oil sands, bitumens and heavy oils*, (1989) ed. L.G. Hepler and C. Hsi, Alberta Oil Sands Technology and Research Authority, Edmonton.

Wallace, D., Starr, J., Thomas, K.P., and Dorrence, S.M. Characterization of oil sand resources, (1988) Alberta Oil Sands Technology and Research Authority, Edmonton.

Wallace, D. (ed.) A review of analytical methods for bitumens and heavy oils, (1988) Alberta Oil Sands Technology and Research Authority, Edmonton.

Wood, P., and Hepler, L.G. Unpublished.

Xu, Y., and Hepler, L.G. Henry's law constants and thermodynamic properties of gases and vapours in bitumens, *Can. J. Chem. Eng.* (1990) 68, 1024–1032.



# APPENDIX

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# 3

## *Standard Laboratory Operating Procedures*





# **I N D E X**

## **I. BATCH EXTRACTION EXPERIMENTS**

- I.1 Sampling, homogenization, and storage of oil sand
- I.2 Oil sand analyses
- I.3 Sub-sampling of oil sand
- I.4 Standard batch extraction procedure
- I.5 Data work-up from batch extraction
- I.6 Sub-sampling of process samples for full work-up experiments

## **II. PROCESS SAMPLE ANALYSES**

- II.1 Basic species determinations
- II.2 CETAB analysis for sulfonate surfactants
- II.3 CETAB analysis for total surfactants
- II.4 Electrokinetic measurements on dispersed samples

## **I. BATCH EXTRACTION EXPERIMENTS**

### **I.1 Sampling, Homogenization, and Storage of Oil Sand**

This method is used to homogenize bulk oil sand samples. The sample is homogenized through a sequence of chopping, quartering, and mixing procedures.

#### **Materials:**

1. Polyethylene sheet — approximately 2 m square and 150  $\mu$ m thickness.
2. Quadro Comil.

#### **Procedure:**

1. Fill 4  $\times$  20 L plastic pails with oil sand from the pile. Sample several locations and take one shovelful from each location for each pail.
2. Chop the oil sand, including clay lumps, through the Quadro Comil.
3. Homogenize the combined 4 pails of oil sand by spreading on the polyethylene sheet and mixing:
  - bag one pail into individual (500 + g) plastic bags.
4. Transfer to new polyethylene pails, seal, and place in cooler at  $-30^{\circ}\text{C}$ .

### **I.2 Oil Sand Analyses**

1. Analyze the oil sand for oil/water/solids (OWS) by the standard soxlet extraction procedure.

Analyze the solids from the soxlet extractor for particle size distribution (PSD) and for metals by atomic emission (AE). Standard procedures for these analyses may be found in "Syncrude Analytical Methods for Oil Sand and Bitumen Processing," edited by J.T. Bulmer and J. Starr.

2. Prepare a water extract of the oil sand as follows:
  - a. Weigh 100 g oil sand into 250 mL beaker.
  - b. Add 100 mL of 80°C deionized water and stir to slurry.
  - c. Wait 5 minutes.
  - d. Decant water into 40 mL plastic centrifuge tubes and spin at 20,000 rpm for 20 minutes.
  - e. Decant off supernatant and ultrafilter through 5000 nominal molecular weight filter.
  - f. Measure and record pH (at room temperature).
  - g. Divide the sample into two parts and analyze one sub-sample for metals by AE and analyze the other sub-sample for anions (sulfate and chloride) by ion chromatography.

### **I.3 Sub-sampling of Oil Sand**

1. Always keep the pails of oil sand in the -30°C cooler.
2. Remove 600–700 g of oil sand for each planned BEU run for the day.
3. Allow the oil sand sample(s) to equilibrate to ambient temperature in lab for about 2 hours.

### **I.4 Standard Batch Extraction Procedure**

1. Check the H<sub>2</sub>O level in bath. Refill if necessary.
2. Switch on the unit. Allow it to warm up to 82°C.
3. Heat 1500 mL H<sub>2</sub>O (deionized) to 82°C.
4. Weigh out 500.0 ± 0.1 g of oil sand.
5. Weigh out the chemical additive to be added. Record weight.

6. Add heated deionized H<sub>2</sub>O (82°C) for a total addition weight of 150 g, i.e., Slurry H<sub>2</sub>O + additive. Record weight.
7. Raise pot into position and turn on impeller to 0.6 on scale (600 rpm).
8. Add oil sand. Mix by raising and lowering the pot to enable the impeller to contact as much of the slurry as possible.
9. Adjust pot to find "lock" position.
10. Turn on air valve. Rotometer setting of 4 (150.0 mL/min).
11. Start timer. Mix for 10 minutes (slurry step).
12. Stop air flow.
13. Add 900 g of 82°C deionized H<sub>2</sub>O. Weigh and record.
14. Mix for further 10 minutes (no air).
15. Stop impeller. Skim off primary froth into a pre-weighed 4 oz jar. Weigh and record total weight.
16. Set air flow at 2 (50.0 mL/min) and impeller to 0.8 (800 rpm).
17. Mix for 5 minutes.
18. Turn off air. Stop impeller.
19. Skim off secondary froth into a pre-weighed 4 oz jar. Weigh and record total weight.
20. Open bottom valve. Drain contents of pot into a pre-weighed 2000 mL beaker.
21. Rinse out sand with deionized H<sub>2</sub>O. (Use a minimum quantity of rinse H<sub>2</sub>O from a pre-weighed wash bottle). Calculate amount of water used.
22. Allow sand to settle for 1 minute.
23. Decant aqueous layer (secondary tailings) into a 1500 mL pre-weighed beaker. Weigh and record.
24. Weigh the 2000 mL beaker and contents (primary tailings) and record.



25. Attach shroud, ensuring proper ventilation by elephant trunk.
26. Remove bottom drain plug from pot. Attach collar and collection jar (400 mL). Wash the shaft and impeller and walls of pot with a toluene/isopropanol mixture. Wash plug and spatula. Collect all washings.
27. Flush all washings into same jar ("wall froth").
28. Disassemble impeller assembly (bottom). Clean inside impeller shaft with brush. Make sure sparging holes are clear.
29. Label samples and submit for analysis unless other subsampling is required; see Section I.7.
30. Record in lab book:
  - a. all observations regarding slurry texture, state of aeration, ease of froth collection, etc.
  - b. any changes to the standard procedures
  - c. a table showing each sample's identity, weight, and tag number.

## **I.5 Data Work-up from Batch Extraction**

Upon receipt of analytical results, use either lab book or computer to:

1. Tabulate results for each BEU sample
2. Calculate mass balances
3. If bitumen mass balance is not within specification (usually 3%), check that data were recorded properly, check analyses, etc.

## **I.6 Sub-sampling of Process Streams for Surfactant and Electrokinetic Mobility Determinations**

1. Save approximately 2 g of primary froth for electrophoretic mobility determinations (weigh and record weight).

2. Save about 30 mL of whole secondary tailings in a 125 mL jar for electrophoretic mobility determinations (weigh and record weight).
3. Centrifuge tailings from BEU. Use 40 mL plastic tubes. Centrifuge at 20,000 rpm for 20 to 30 minutes. Do 2 batches of 8 tubes.
4. Reconstitute the tailings sample by cleaning the centrifuge tubes with toluene and water. Partly fill the tubes with toluene and water and place on the shaker to clean the tubes. Transfer back to original beaker and submit samples for OWS.
5. Ultrafilter the centrifugate using a 5000 nominal molecular weight filter.
6. Submit a 10 mL sample of the ultrafiltered tailings for metals analysis by AE.
7. Submit a 25 mL sample of the ultrafiltered tailings for chloride and sulfate by ion chromatography.
8. Calculate the concentration of  $\text{Na}_2\text{SO}_4$  according to the equation below. This concentration is used in the CETAB analysis.

$$[\text{Na}_2\text{SO}_4] = \frac{\text{Concentration } \text{SO}_4^{2-} \text{ (ppm)}}{96} \text{ mmoles/L}$$

For example, if  $[\text{SO}_4^{2-}]$  is reported at 140 ppm:

$$[\text{Na}_2\text{SO}_4] = \frac{140}{96} = 1.45 \text{ mmoles/L}$$

9. Calculate the concentration of NaCl:

$$[\text{NaCl}] = \frac{\text{Concentration } \text{Cl}^- \text{ (ppm)}}{35.5} \text{ mmoles/L}$$

For example, if  $[\text{Cl}^-]$  is reported at 125 ppm:

$$[\text{NaCl}] = \frac{125}{35.5} = 3.52 \text{ mmoles/L}$$

## II. PROCESS SAMPLE ANALYSES

The objective of this procedure is to determine carbonate and bicarbonate in the tailings water sample. The procedure involves a titration on the ultrafiltered tailings water (as received) with standard hydrochloric acid. If the sample contains carbonate and bicarbonate, two end points will occur — one at  $\text{pH} \approx 7.5$ , which is the carbonate end point, and a second one at  $\text{pH} \approx 4.5$ , which is the bicarbonate plus carboxylate end point. If the sample does not contain carbonate, then only one end point will be obtained at  $\text{pH} \approx 4.5$ .

The data that are needed to prepare the CETAB standards are carbonate concentration and approximate bicarbonate concentration. It is necessary to subtract the carbonate concentration from the bicarbonate to get the true bicarbonate concentration because carbonate at the end of the first end point has become bicarbonate and titrates again and is included in the second end point.

The detailed procedure is as follows:

1. Measure initial pH and conductivity on the ultrafiltered tailings water sample.
2. Titrate a 10 mL sample of ultrafiltered tailings water with standard 0.006 N HCl. Read two end points. First end point = amount of HCl to get end point at  $\text{pH} \approx 7.6$ . Second end point = amount of HCl to get from first end point to end point at  $\text{pH} \approx 4.5$ . If sample is too large or too small, repeat the titration with another sample size.
3. Calculate the concentrations of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  in mmoles/L:

$$[\text{Na}_2\text{CO}_3] = \frac{\text{mL HCl at first E.P.} \times \text{N HCl} \times 1000}{\text{Sample Volume}} \text{ mmoles/L}$$

$$[\text{NaHCO}_3] = \frac{\text{mL HCl (2nd E.P. - 1st E.P.)} \times \text{N HCl} \times 1000}{\text{Sample Volume}} \text{ mmoles/L}$$

Typically:

$$[\text{Na}_2\text{CO}_3] \approx 0.20 \text{ mmoles/L}$$

$$[\text{NaHCO}_3] \approx 2.80 \text{ mmoles/L}$$

## **II.2 CETAB Analysis for Sulfonate Surfactants**

This procedure is designed to measure the concentration of surface active sodium sulfonates in the tailings water sample. The surface active sodium sulfonates are reacted (titrated) with surface active cetyltrimethylammonium bromide (CETAB) to form a highly surface active complex. The titration is monitored by following surface tension of the titration mixture, with the total drop in surface tension being proportional to concentration. The concentration of the sodium sulfonate unknown is found by matching the unknown titration curve to standard titration curves obtained using known concentrations of sodium octyl sulfonic acid (NaOSA). It is necessary to use the same salt concentrations ( $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ ,  $\text{NaCl}$ , and  $\text{Na}_2\text{SO}_4$ ) for the standard samples as in the unknown samples because the decrease in surface tension due to the complex is to some extent dependent on the salt concentration in the solution.

The titration is done at  $\text{pH} \approx 3$  because the other surface active species present (sodium carboxylates) are in their non-surface active acid form at this pH. Sulfonates, however, are still in their surface active form at  $\text{pH} \approx 3$  and consequently can be measured without also measuring sodium carboxylates.

The titration is done using a Sensodyne 5000 tensiometer (Chemical Dynamics) fitted with a jacketed 200 mL titration cell operated at  $40^\circ\text{C}$ .

1. Clean the instrument glass probes by immersion in sequence in water, acetone, toluene, methanol, and water (use 20 dips in the fluids for each rinse).
2. Take 40 mL of ultrafiltered tailings water and adjust pH to 3.0 with dilute HCl. A precipitate will form and the solution will become cloudy.
3. Hold at room temperature for at least 15 minutes.
4. Filter the solution through 0.45  $\mu\text{m}$  filter paper.
5. De-gas the solution with a stream of nitrogen for one hour.
6. Do a CETAB titration on 25 mL of the above sample. Place the sample in the cell and dilute to 50 mL. Add 0.1 mL increments of 0.005N CETAB. Stir 1 minute and hold 3 minutes before reading surface tension after each addition of CETAB.

7. Prepare a  $\text{pH} \approx 3.0$  standard (40 mL). Prepare a standard that contains the same concentration of  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{NaCl}$  (see section I.6 for determination of sulfate and chloride concentrations in the sample) as the sample and that contains a low concentration of sodium octyl sulfonic acid ( $\text{NaOSA}$ ), say 0.05 mmoles/L.

For example:

WANT	1.00 mmoles/L $\text{NaCl}$
	3.24 mmoles/L $\text{Na}_2\text{CO}_3$
	5.09 mmoles/L $\text{NaHCO}_3$
	1.45 mmoles/L $\text{Na}_2\text{SO}_4$
	0.05 mmoles/L $\text{NaOSA}$

Make up stock solutions as follows:

$$[\text{Na}_2\text{CO}_3] = 20 \text{ mmoles/L}$$

$$[\text{NaHCO}_3] = 30 \text{ mmoles/L}$$

$$[\text{NaCl}] = 40 \text{ mmoles/L}$$

$$[\text{NaCl}] = 10 \text{ mmoles/L}$$

$$[\text{Na}_2\text{SO}_4] = 20 \text{ mmoles/L}$$

$$[\text{Na}_2\text{SO}_4] = 10 \text{ mmoles/L}$$

$$[\text{NaOSA}] = 10 \text{ mmoles/L}$$

Use the relationship  $N_1V_1 = N_2V_2$  to do calculations for preparation of the standard.

For example for  $\text{NaHCO}_3$ :  $N_1V_1 = N_2V_2$

$$30.0 V_1 = 5.09 \times 40 \text{ mL}$$

$$V_1 = 5.09 \text{ mL}$$



For example for NaOSA:  $N_1 V_1 = N_2 V_2$

$$10 V_1 = 0.05 \times 40 \text{ mL}$$

$$V_1 = 0.20 \text{ mL}$$

Measure the calculated quantities and dilute to 40.0 mL with deionized water.

8. Adjust pH of the standard to 3.0. Hold at least 15 minutes. Filter (0.45  $\mu\text{m}$ ) and do CETAB titration on 25 mL.
9. Prepare a standard containing salts only (i.e., no NaOSA), adjust pH to 3.0, hold at least 15 minutes, filter (0.45  $\mu\text{m}$ ), and do a CETAB titration on 25 mL.
10. Compare standard CETAB curves to the sample CETAB curve. Compare curves by matching graphs (i.e., line up the point at surface tension 72 on one graph with the point at surface tension 72 on the other graph) and compare the regions of the curves from about 0.6 mL CETAB to about 1.4 mL CETAB. Normally the sample curve will lie somewhere between the 0.00 NaOSA and the 0.05 NaOSA curve. Estimate the correct concentration and prepare and run a standard at this concentration. For example, if the distance between no NaOSA and 0.05 mmoles/L NaOSA on the graph at 1.0 mL of CETAB is 10 mm and the distance between no NaOSA and the sample at 1.0 mL of CETAB is 8 mm, then the correct concentration of NaOSA is

$$[\text{NaOSA}] = \frac{0.05 \times 8}{10} = 0.04 \text{ mmoles/L}$$

### II.3 CETAB Analysis for Total Surfactants

This procedure is similar to the procedure at  $\text{pH} \approx 3$ , but is designed to measure the total of carboxylate surfactant plus sulfonate surfactant, which are both in their surface active form at  $\text{pH} \approx 8.5$ . The unknown titration curves are compared to standard titration curves obtained using commercial naphthenic acid (CNA).

1. Clean probes as per section II.2, step 1.

2. Prepare standard. The standard should contain the same concentrations of  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{NaCl}$  as the  $\text{pH} \approx 3$  standard. It should contain 0.05 mmoles/L of CNA.

For example:

WANT             $[\text{Na}_2\text{CO}_3] = 3.24 \text{ mmoles/L}$

$[\text{NaHCO}_3] = 5.09 \text{ mmoles/L}$

$[\text{Na}_2\text{SO}_4] = 145 \text{ mmoles/L}$

$[\text{CNA}] = 0.05 \text{ mmoles/L}$

Have             $[\text{CNA}] = 4.21 \text{ mmoles/L}$

Use             $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ , and  $\text{Na}_2\text{SO}_4$  as at  $\text{pH} \approx 3.0$

and CNA         $N_1 V_1 = N_2 V_2$

$4.21 V_1 = 0.05 \times 40 \text{ mL}$

$V_1 = 0.47 \text{ mL}$

3. Do a CETAB titration on 15 mL of standard.
4. Do a CETAB titration on the 15 mL sample.
5. Compare sample curve to standard curve. Line up 72 on standard to 72 on sample curves. Compare curves in the region from about 0.6 mL CETAB to 1.4 mL CETAB.
6. If the sample curve is shallower than the standard curve, prepare and titrate (15 mL) a standard at 0.00 CNA. If the sample curve is steeper than the standard curve, prepare and titrate (15 mL) a standard at 0.15 mmoles/L CNA.
7. Compare curves and estimate correct standard concentration. Prepare a standard at the estimated CNA concentration and titrate 15 mL. This curve should match the sample curve in the region of 0.6 mL CETAB to 1.2 mL CETAB.

## **II.4 Electrokinetic Measurements on Dispersed Samples**

Samples obtained from BEU experiments:

1. ~ 2 g primary froth.
2. 20 mL in 4 oz jar secondary tailings (whole).
3. 100 mL in 4 oz jar ultrafiltered tailings.
  - Measure electrophoretic mobilities of dispersed bitumen drops and fine solids as detailed in following sections.

General:

- Instrument set-up is per instrument manual. The instrument is a Rank Brothers Mark II.
- Operating procedure is per instrument manual. Palladium electrodes should be cleaned and charged with H<sub>2</sub> DAILY. Water bath should be set at 25°C.

Electrophoretic mobility of fine solids:

1. Take about 25 mL of the ultrafiltered sample and add about 3 drops of (whole) secondary tailings suspension, mix.
2. Fill electrophoresis cell, fix in holder, place palladium electrodes in the cell.
3. Adjust viewing system so optics are focused on the near (to the camera) stationary plane in the cell (procedure in instrument manual) record measurements used for plane location.
4. Initialize rotating prism/microprocessor (see instrument manual).
5. Set prism to a reasonable speed (ca. 20–40 oscillations/minute).
6. Switch on electrode voltage and adjust particle movement to match the moving grid, read voltage, switch electrodes off.
7. Record speed and voltage; repeat above step 3 times.

8. Repeat above 3 steps 4 times, each with new speed settings. Try to keep speeds in 20–40 oscillations/minute range and voltages under 100 V (preferably 30–80 V).
9. Calculate electrophoretic mobilities according to instrument manual procedure.

**Electrophoretic mobilities of bitumen drops:**

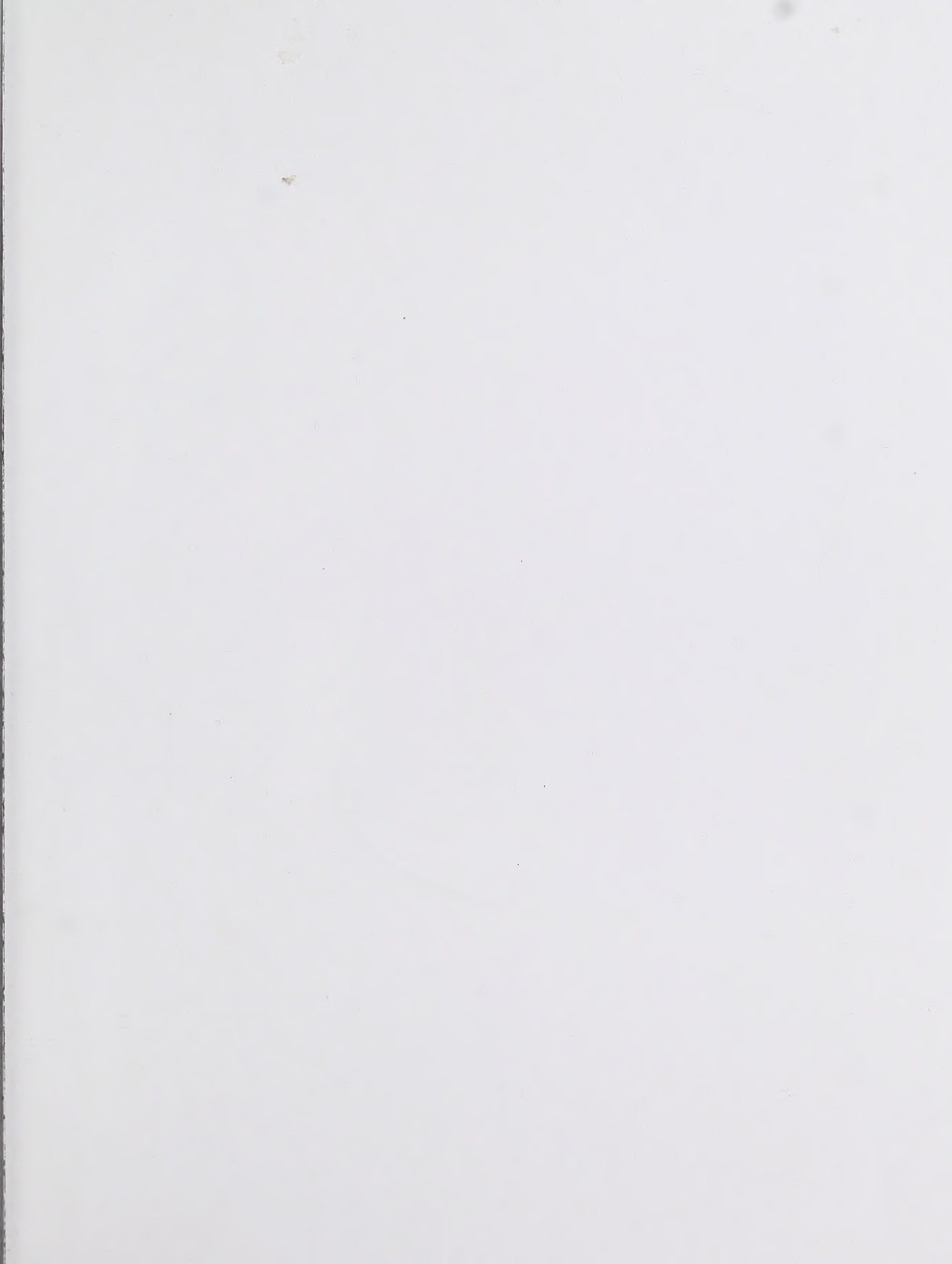
1. Take about 50 mL of the ultrafiltered sample; place about 1–2 g of the primary froth in this sample; place the Braun sonifier probe in the sample (well immersed), turn the sonifier on, set at 200 W and 5 minutes.
2. The sonified sample should contain small (about 10  $\mu\text{m}$ ) drops of bitumen. Use the cell in the instrument to confirm that the drops are about 10  $\mu\text{m}$  in size; sonify for an additional 5 minutes if needed.
3. Fill electrophoresis cell, fix in holder, place palladium electrodes in cell.
4. Adjust viewing system, prism, and microprocessor as in fine solids procedure.
5. Using applied voltages and moving prism, measure droplet speeds and voltages, and record, as in fine solids procedure.
6. Be careful to measure only droplets that are in sharp focus at the near stationary plane and that are of about 10  $\mu\text{m}$  diameter.
7. Calculate electrophoretic mobilities according to instrument manual procedure.

















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